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March 27, 1957

Dear Sir:

Encls
Enclosed is the Summary Report on Task Order No. 6, describing the results of the research conducted during the period from May 29, 1956, through January 28, 1957.

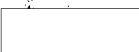
We are quite enthusiastic about the preliminary design of the hydrogen generator that has been conceived because it appears to fulfill the specified requirements so completely. In accord with our recent discussions, we have prepared a proposal describing a program directed toward the design, construction, and evaluation of a prototype generator unit and have mailed it to you as of this date.

We would appreciate any comments that you or your associates might care to make with regard to the research performed under Task Order No. 6.

Sincerely,



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Enclosure

In Triplicate

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SUMMARY REPORT

ON

TASK ORDER NO. C

January 28, 1957

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SUMMARY REPORT

on

TASK ORDER NO. C

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January 28, 1957

INTRODUCTION

This report presents a detailed account of the studies directed toward the development of a large-scale, hydrogen generator under Task Order No. C, and describes the design recommended and the materials required for a prototype generator.

The objectives of Task Order No. C included:

- (1) Conducting a literature search on and a comparison of hydrogen-generator types, particularly on the basis of the underlying generation reactions, and selecting the particular reaction or reactions that were considered to be of major interest.
- (2) Performing laboratory research to obtain design data not otherwise available relative to the most applicable generation reaction.
- (3) Conducting a preliminary design analysis of a hydrogen generator that would satisfy the specified requirements.

A Topical Report^{(1)*} prepared under Task Order No. C presented an analysis of the various reaction systems for producing hydrogen to meet the

*Numbers in superscript refer to items listed under References.

Note: The data on which this report is based are recorded in our Laboratory Record Book No. 12024, pp 1-89; No. 12268, pp 1-81; No. 12321, pp 1-12; and No. 12344, pp 1-100.

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requirements of the desired generator. The catalysed hydrolysis of sodium borohydride was selected for further research and development. The present report describes the experimental development of the "two-solution", CoCl_2 -catalysed hydrolysis of NaBH_4 for the purpose of generating 3,500 cu ft of hydrogen under controlled conditions.

The research summarized in this report was conducted during the period from May 29, 1956, through January 28, 1957.

SUMMARY AND CONCLUSIONS

On the basis of these studies, a hydrogen generator that meets the specified requirements would have the following general characteristics: The generator would contain a "pool" of a solution of sodium borohydride in alkaline water (0.01M NaOH). A cobaltous chloride solution (CoCl_2) would be added to the borohydride solution to catalyze the hydrolysis of the borohydride and start hydrogen generation.

Specific details relative to the hydrolysis reaction in and the proposed design for the full-scale generator, operating under the specified conditions, are as follows:

Pool dimensions	1.5 ft in depth x 50 sq ft of surface area
Initial temperature	72 F (22 C)
Hydrolysis solution (0.1M NaOH):	
Water	560 gal
NaBH_4 (98% pure)	100 lb
NaOH	0.2 lb

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Catalyst solution	2.4 lb CoCl_2 in 10 gal H_2O
Capacity	3,700 cu ft H_2 in 45 to 60 min
Highest temperature of off-gas	130 F (54 C)
Proposed generator:	
Diameter	8 ft
Height	33 in.
Approximate weight	50 lb
Approximate Total Weight (generator + chemicals):	158 lb.

Studies with natural waters have shown that impurities in these waters, not specifically identifiable, cause about a 20 per cent reduction in the generation rate. The advisability of making the waters used basic before dissolving the sodium borohydride has also been established in the natural-water studies.

Kinetic studies have indicated that the rate constant for the catalyzed hydrolysis is proportional to the concentration of the catalyst, and that the temperature coefficient, or activation energy, for this reaction is approximately 17,500 calories per mole. Preliminary deductions on the reaction kinetics have been made, and, on the basis of several calculated rate curves, it has been shown that an increase in the initial temperature of 9 F (5 C) will decrease the time for complete reaction under adiabatic conditions by about 50 per cent. These calculations also indicate that small errors in making up the borohydride and catalyst solutions will cause very minor effects on the generation rate, but will influence the final temperature of the off-gas.

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REACTION SYSTEMS FOR GENERATING HYDROGEN**Specifications for the Proposed Generator**

Since the specifications for the hydrogen generator were important in the formulation of the various studies in this program, they are listed here in detail:

(1) Capacity. Enough hydrogen to provide a minimum of 250 lb of lift at sea level; this is equivalent to approximately 3,500 cu ft of hydrogen. Presumably, the purity of the hydrogen (air and water content) is less important for the intended application than is the case with hydrogen for meteorological balloons, which must rise at a predictable rate.

(2) Rate. Total capacity to be generated at a controlled rate within 1 hour once the reaction is started.

(3) Pressure. Low; slightly above atmospheric pressure at the outlet of the generator.

(4) Ambient Temperature. Not stated. Tentatively, a range of 32 to 120 F is assumed; lower temperatures would necessitate the addition of nonaqueous solvents to the solution.

(5) Temperature of Off-Gas. Not stated, except that the temperature must not be high enough to damage a balloon made of 2- or 2-1/2-mil polyethylene. Any temperature below 212 F (100 C) should be safe for conventional polyethylene.

(6) Maximum Weight. A total of 500 pounds or less for all components and chemicals, except water. Any possible reduction below this maximum would be desirable.

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(7) Construction. Low radar detectability; unitized components (each 50 pounds or less) which could be carried and assembled by one man. In general, the construction should be rugged.

(8) Operation. Operation by one nontechnical operator. Once hydrogen generation begins, the operator will be occupied with the handling of the balloon, so that foolproof, self-controlled operation with automatic safety controls will be needed. Materials and chemicals should be selected to overcome potentially explosive or toxic conditions.

(9) Durability. All components and chemicals designed for safe storage and shipment without inspection or attention for periods of many months. The generator should be designed for a single one-hour operating period, with recharging and reuse not contemplated.

(10) Auxiliary Power and Materials at Operating Site. Completely self-contained unit. Only water would be available in reasonable quantities at the site. The water will probably not be sea water; there will probably be a small lake, a large pond, or a flowing stream to provide the water. The generator might conceivably be set directly in the water for operation. The water temperature may vary from 40 to 90 F, but the limits are likely to be 50 to 70 F.

Materials for a Self-Contained Generator

In order for the generator to meet the requirements of being self-contained and self-generating, hydrolyses which proceed at uniform rates and which go to completion, or approximately so, were the preferable type of basic reaction.

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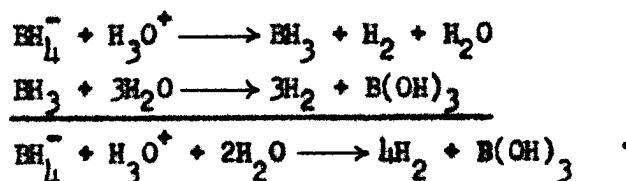
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Table 1 indicates various materials which will yield hydrogen upon hydrolysis. The system which appeared to lend itself best to this development was the catalysed hydrolysis of sodium borohydride; a detailed discussion of this is presented in Reference 1. Initially, potassium borohydride was considered also. The hydrolysis of sodium borohydride was reported to produce large amounts of foam during high rates of generation⁽²⁾, and there was reason to believe, early in this study, that potassium borohydride, which might be produced in greater purity, might foam less.

Characteristics of the Sodium and
Potassium Borohydride Systems

Sodium and potassium borohydrides form relatively stable aqueous solutions when cold, although both hydrolyse slightly on standing. Stable solutions of these borohydrides are achieved at pH values greater than 7, but preferably at a pH of the order of 10 to 12.

The hydrolysis of borohydride solutions may be achieved by acidification in aqueous solution or by catalysis. The acidification reaction probably occurs in the following manner:



The catalysed reaction, rather than forming boric acid, yields the metaborate ion:

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TABLE 1. POSSIBLE MATERIALS FOR A SELF-CONTAINED, SELF-GENERATING SYSTEM
(For production of 3,500 cu ft of hydrogen)

Material	Minimum Weight, lb	Applicability	Comments
Lithium borohydride (LiBH_4)	53.4	No	Unsafe. May ignite on contact with water.
Lithium hydride (LiH)	77.5	Possible	Some danger of ignition in presence of moisture. Powdered material must be stored in sealed containers under inert atmosphere. Large lumps react slowly with water (reaction is heterogeneous).
Sodium borohydride (NaBH_4)	92.7	Yes	Acid or proper catalyst required for complete reaction.
Potassium borohydride (KBH_4)	132.2	Yes	Similar to NaBH_4 , but reaction is milder.
Calcium hydride (CaH_2)	205.3	Possible	Has been used in generators. Weight requirement is high.
Sodium hydride (NaH)	234.2	No	Ignites on contact with water.
Metals (i.e., Na, K, Ca, Zr, etc.)	-	No	Unsafe due to explosion hazards and lack of control.

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Schlesinger and co-workers⁽³⁾ and the Ethyl Laboratories⁽²⁾ have studied the hydrolysis of sodium borohydride in some detail. Schlesinger reports that the hydrolysis is dependent only on the pH of the system and is independent of the specific acids and salts used to buffer the solution. A number of acids can be used for the acid-accelerated hydrolysis. In Table 2 of Reference 1, 24 accelerators used by Schlesinger were listed. Boric oxide was reported to be the best acid accelerator. This was based on the requirements of the Ethyl Laboratories and the ability of a boric oxide - sodium borohydride mixture, in the molar ratio 1:2, to hydrolyze completely in 10 min.

The hydrolysis may be catalyzed by a number of metal salts. In Table 3 of Reference 1, more than 50 catalyst materials were given, and probably the list could be expanded further. The catalyst materials were separated into three groups - those which effect a very slow hydrolysis, those which effect a slow or incomplete hydrolysis, and those which effect a fast and apparently complete hydrolysis. As was pointed out in the analysis in Reference 1, cobaltous chloride, which is in the third group - fast catalysts, appeared to be the preferable catalyst for this program.

A more complete review of these reactions is presented in Reference 1.

GENERAL OBJECTIVES OF THE EXPERIMENTAL PROGRAM

In order to use the cobaltous chloride - catalyzed hydrolysis of sodium borohydride to generate hydrogen, additional information was needed and this was obtained from studies of the following factors:

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- (1) The feasibility of the two-solution system.
- (2) The combined effect of the concentration of CoCl_2 and NaBH_4 on the rate of hydrolysis. Implicit in this consideration was the completeness of reaction.
- (3) The influence of scaling factors.
- (4) The effect of the initial water temperature on the rate of reaction. This was important because of variations that would be encountered in the water temperature under field conditions.
- (5) The effect of natural waters on the rate of reaction. Since ground water is to be used, inorganic and organic contaminants in natural waters may exert catalytic effects on the hydrolysis.

The results of these studies are described below.

DEFINITIONS AND CONVENTIONS

In this report, the temperatures are generally reported in degrees C and gas volumes have been reduced to standard conditions. In general, c-g-s units are used; however, when hydrogen volumes are much larger than 1 liter, they are given in cu ft.

Charge sizes refer to the amount of hydrogen that can be generated from the selected weight of borohydride. Since 1 mole of sodium borohydride will generate 4 moles of hydrogen, the following conversions will be useful:

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$$\begin{aligned}
 11.98 \text{ g NaBH}_4 (0.317 \text{ mole}) &\equiv 1 \text{ cu ft H}_2 \\
 &\equiv 28.32 \text{ liters H}_2 \\
 &\equiv 1.26 \text{ moles H}_2.
 \end{aligned}$$

Sodium borohydride concentrations are reported in moles NaBH₄ per liter of solution*.

The cobaltous chloride concentrations referred to represent the molar ratios of anhydrous CoCl₂ to NaBH₄*.

In descriptions of the reactors, especially in the large-scale studies, a reactor is often referred to, for example, as a 4.1-cu-ft unit. The "4.1 cu ft" represents the size of the charge, expressed as available hydrogen, loaded into such a reactor.

Hydrogen-generation rates in the small- and large-scale studies are expressed as specific rates, $R_{sp}(t)$. The specific rate, which is an "average" rate per unit charge expressed as available hydrogen, is therefore the reciprocal of the time, in minutes, necessary to achieve complete reaction. For convenience, the data are analyzed on the basis of a total generation time of 50 min, i.e.,

$$R_{sp}(50) = \frac{\text{H}_2 \text{ evolved in 50 min}}{(\text{Total H}_2 \text{ in charge})(50 \text{ min})} = \text{min}^{-1}.$$

*In the Task Order No. C monthly letter reports and in the Ethyl report⁽²⁾, different conventions were used. The monthly letter reports used W (g solution per g BH₄⁻ ion) and C (g CoCl₂ per 100 g BH₄⁻ ion). The Ethyl report used R (g water per g NaBH₄) and % (g CoCl₂ per 100 g NaBH₄).

The conversion factors relating these conventions are as follows:

$$1W = 0.402 R = 67.57 \text{ moles NaBH}_4/\text{liter solution}$$

$$1C = 0.402 \% = 0.00114 \text{ mole CoCl}_2/\text{mole NaBH}_4.$$

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Thus, $R_{sp}(t)$ for 100 per cent reaction is simply one divided by the time required. It must be recognized that R_{sp} presents only a partial picture of the generation rate and gives no indication as to the shape of the rate curve with respect to time.

EXPERIMENTAL METHODS

Apparatus and Materials

Experimental studies were conducted in a variety of reactors including 50-ml flasks, 250-ml graduates, 1-gallon Mason jars, and cylindrical reactors of various sizes up to approximately 10 in. in diameter by 3 ft in height. Each reactor was provided with an opening through which the catalyst solution was added, a gas outlet, and a thermocouple well. Calibration marks on the reactor made it possible to estimate the volume of foam produced during the reaction.

Temperatures were measured by means of a single-junction copper-constantan thermocouple. Barometric pressures were read on an aneroid barometer.

Experiments with 1-liter charges were performed in a 250-ml graduate, and the hydrogen was collected over water in a 1-liter calibrated gas burette. Charges in the range of 0.5 to 3.5 cu ft of hydrogen were reacted in a 1-gallon jar, approximately 9 in. in height x 5-1/2 in. in diameter. The hydrogen was metered through a wet-test meter and released to a hood. Except as stated, the reactions were run under ambient conditions of temperature and pressure.

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For charges larger than 3.5 cu ft of hydrogen and for the relatively large scaling studies, four cylindrical reactors, each 3 ft high and of varying diameters, were constructed. The dimensions and charge sizes of these reactors are as follows:

<u>Diameter</u>	<u>Charge Size</u>
1.9-in.	1.4 cu ft of hydrogen
2.7-in.	3.1 cu ft of hydrogen
5.5-in.	11.4 cu ft of hydrogen
9.8-in.	36.4 cu ft of hydrogen

The first three reactors were constructed of Pyrex glass and the last reactor was made from an acrylic resin.

Figure 1 shows a diagram of the largest experimental-reactor setup in which, after the cobalt chloride catalyst was added to the reactor, the hydrogen was passed through the wet-test meter.

The sodium borohydride used in these studies was obtained from Metal Hydrides, Inc., and the Callery Chemical Company. The products from both companies are supplied 98 per cent pure, and were used with no further purification. The Metal Hydrides product was stated to contain the following impurities: sodium methylete, sodium hydroxide, and perhaps borates. The Callery Chemical Company product had a higher bulk density than the Metal Hydrides product, and also had an "amine like" odor. However, both products behaved similarly in these studies.

The potassium borohydride, obtained from Metal Hydrides, was 97 per cent pure, with probably the same impurities as the sodium salt.

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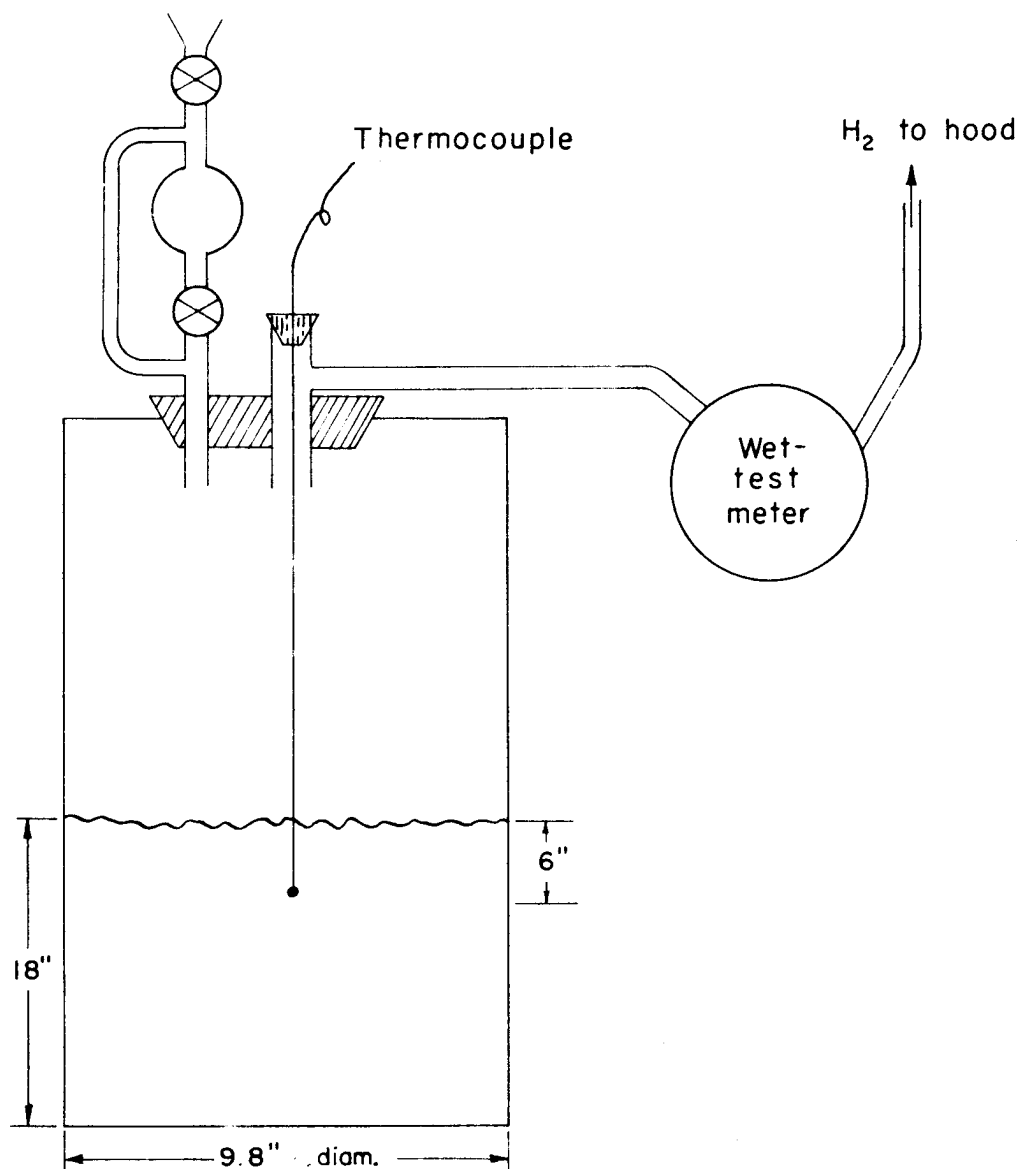


FIGURE 1. DIAGRAM OF REACTOR SETUP

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The cobaltous chloride used was Baker Analyzed Reagent, 99.9 per cent $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. This salt was also used with no further purification.

General Procedure

In the performance of the hydrolysis experiments, the borohydride solution was placed in the reactor, and the catalyst solution in a separatory funnel. At first, the concentrations of the solutions used were based on the final volume of mixed solution. After several experiments, attempts were made to maintain a constant value of approximately 1:30 for the ratio of the volume of catalyst solution added to the volume of borohydride solution.

The initial temperature of the solution was usually recorded, and, if necessary, the internal pressure in the system was adjusted to atmospheric pressure. The stopcock of the separatory funnel was then opened to admit the catalyst solution to the reactor. For the small charges (1 liter of hydrogen), the rate of addition of the catalyst solution appeared to have an effect on the rate of reaction. However, no effect of addition rate was observed with the larger charge sizes, and for these the catalyst solution was allowed to stream into the reactor at the rate determined by the stopcock bore; this took approximately 10 to 20 seconds.

At intervals, readings were taken of the volume of gas generated, the temperature of the solution, and the volume of foam in the reactor. The gas volumes corrected to STP were plotted as a function of time; on the same graph, temperature and foam volumes were also plotted.

Because solutions of borohydride are slightly unstable, they were prepared fresh daily. It is generally stated in the literature that NaBH_4

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dissolves in cold water without an extensive evolution of hydrogen. At room temperature and above, the hydrolysis proceeds more rapidly, but soon slows down and becomes inappreciable due to the increasing alkalinity resulting from the presence of the reaction products. Hoekstra⁽⁴⁾ states that the rate of reaction becomes negligible at a pH greater than 9. However, there is some hydrolysis even in solutions normal in NaOH⁽⁵⁾.

Deionized water was used in most of the experiments, so as to maintain a reproducible solvent.

In general, the reactions were run under ambient-temperature conditions. In a few instances, reactions were also run under partially isothermal conditions, by setting the reactor in a large water bath. The temperature-dependency studies were, of course, performed under controlled isothermal conditions.

EXPERIMENTAL RESULTS

General Observations

The hydrolysis reaction generally occurs as follows: As the CoCl_2 enters the solution in the reaction vessel, a black layer of precipitate, presumably cobaltous boride, forms at the top of the solution and gradually settles toward the bottom. It may take as long as 5 minutes before the entire solution is colored black by the precipitate.

Several features of general interest are best described with reference to the rate curves shown in Figure 2. Figure 2 is a rate curve for the generation of hydrogen in the largest reactor, 36.4 cu ft. The hydrogen

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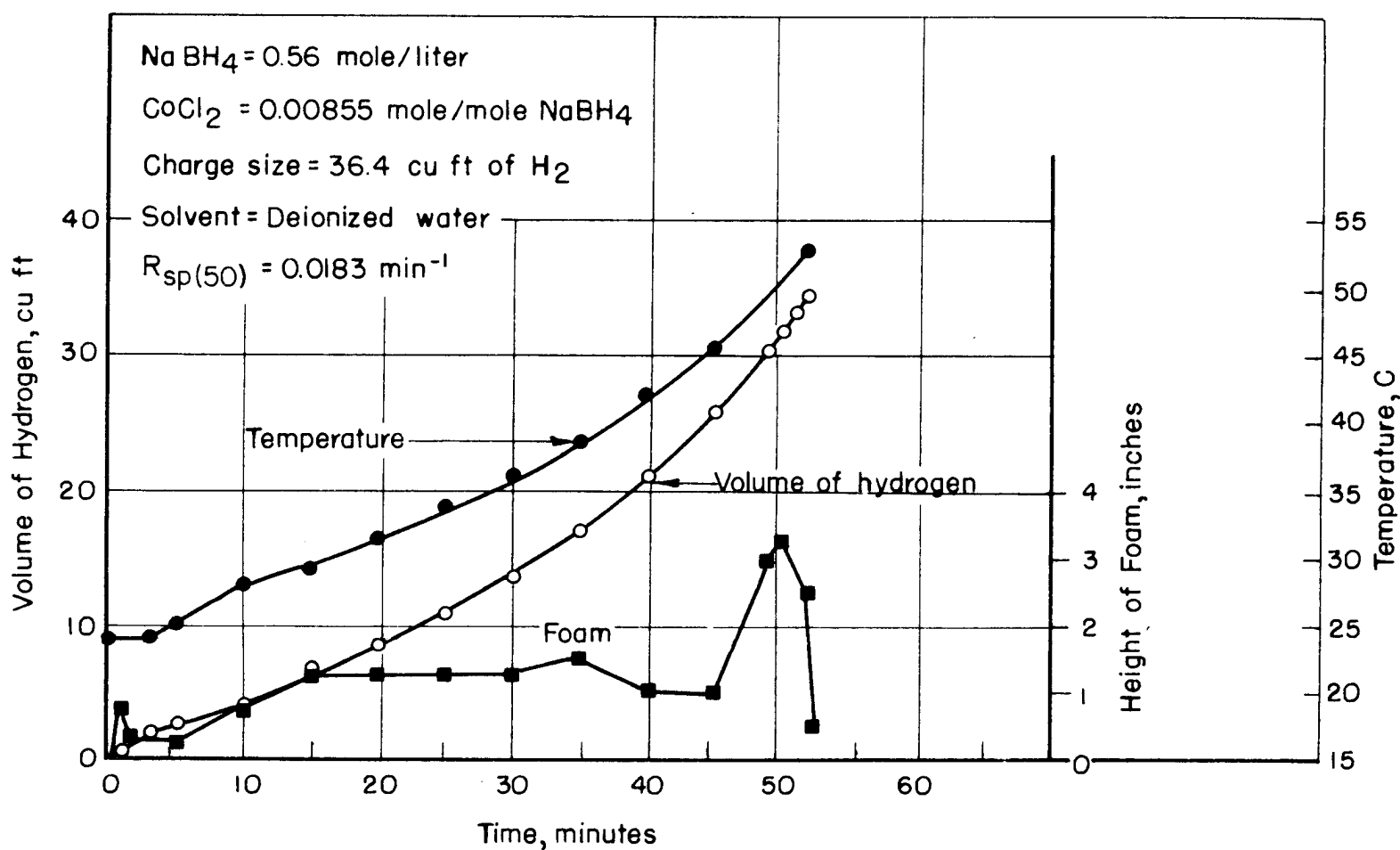
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FIGURE 2. TYPICAL RATE CURVE FOR HYDROGEN GENERATION

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curve indicates that, as soon as the CoCl_2 is added, there is a sudden evolution of hydrogen; this is followed, a few minutes later, by a temperature "jump" of approximately 4 degrees C (7 degrees F). It is also to be noted that a small amount of foam forms at the very start of the reaction. After about 5 minutes, the hydrogen evolves smoothly. As will be shown in some of the kinetic studies described below, this temperature jump is caused by the exothermic formation of the black precipitate. The sudden jump appears to occur several minutes after the reaction has started because the thermocouple, measuring temperature, is located 6 inches below the top of the solution, and thus there is a delay before the thermocouple senses the presence of the warmer portion of the solution at the top of the reaction solution, as it finally mixes with the cooler solution below. The foam curve tends to follow the general shape of the hydrogen and the temperature curves except that, as soon as the reaction is completed, the foam curve drops because the unstable foam collapses.

Feasibility of the CoCl_2 - NaBH_4 System

The analysis in Reference 1 indicated that a two-solution CoCl_2 - NaBH_4 system would be the most desirable system for further research and development in connection with Task Order No. C. Before all of the effort was concentrated on this system, however, it was believed desirable to establish its superiority over other possible systems such as those involving the use of KBH_4 , acid accelerators, or catalysts other than CoCl_2 . In addition, it appeared worth while to establish the optimum method of mixing and the stability of the solutions for a two-solution system.

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Hydrolysis of Potassium Borohydride

It was felt early in the program that, if foaming were a problem as it was in the Ethyl studies⁽²⁾, the advantages of using KBH_4 might outweigh the disadvantage stemming from the larger weight of chemical required. It was the thought that KBH_4 might be obtained in higher purity, and, as a result of the use of purer material, the foaming might be decreased. Actually, the KBH_4 supplied by Metal Hydrides was not purer than the NaBH_4 . It was also found that foaming was not a serious problem in this study. For these reasons, there was no advantage to using the heavier KBH_4 , and no further work was done with it.

Acid Acceleration

Schlesinger⁽³⁾ showed that the hydrolysis of NaBH_4 could be accelerated by many acids, and that stronger acids produced greater acceleration. He also indicated that the rate of generation decreased as the pH of the solution increased. The data reported by Schlesinger, however, were for higher specific rates, $R_{sp} \approx 0.10 \text{ min}^{-1}$, than those of interest to Task Order No. C. It was decided, therefore, to check a few acid accelerators at lower concentrations than were used by Schlesinger.

Table 2 summarizes the results of hydrolysis experiments with malonic, tartaric, and boric acids, and ammonium chloride. The data show that, in general, if the acid concentration is increased, the hydrolysis starts out too rapidly, and if the acid concentration is reduced, complete reaction is never reached.

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TABLE 2. HYDROLYSIS STUDIES WITH ACID ACCELERATORS

(Reaction conditions: NaBH_4 - 0.45 mole/liter; solvent - deionized water; accelerator added to borohydride rapidly, in a continuous stream)

Acid Accelerator	Ratio Acid to NaBH_4 , wt per cent	Charge Size, cc H_2	Hydrogen Evolved, per cent			Total Reaction Time, min
			After 2 min	After 20 min	Final	
Malonic ⁽¹⁾	20	835	24	54	67	42
Malonic	50	876	64 ⁽²⁾	>90	94	34
NH_4Cl	20	893	8.4	37	59	63
NH_4Cl	50	864	18.5	~64	79	45
NH_4Cl	75	722	21	67	78+	36
Tartaric	20	876	24.5	47.5	64	60
B_2O_3	11.7	890	14	40.5	59	59
B_2O_3	50	818	37	76	90	48
B_2O_3 ⁽³⁾	50	859	~4	45	87	74

(1) Added over a 2-minute interval.

(2) 49 per cent evolved after 1/2 minute.

(3) See Figure 1. B_2O_3 (10 ml) added dropwise, 4 drops per min, over a 44-min period.

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Figure 3 shows three rate curves for boric acid - accelerated hydrolyses. The dashed curve in Figure 3 represents data obtained in a special experiment in which the boric acid was added dropwise over a 44-min period. As this curve shows, the generation rate can be regulated by adding acid at a controlled rate.

The general conclusion drawn from these studies, therefore, is that acid accelerators are not applicable to this program since the desired generator is to operate as a self-sustaining system. In addition, a weight of acid almost equal to the weight of NaBH_4 would be required, to exploit acid acceleration.

Catalysts Other Than Cobalt Chloride

Three catalysts were studied to compare the effects of different catalysts with the known effects of CoCl_2 . The catalysts investigated were NiCl_2 , CrCl_3 , and AlCl_3 . The experiments were run on approximately 800-cc (of hydrogen) charges of various sodium borohydride solutions.

The specific-rate data are listed in Table 3. It is apparent that there is no special reason to prefer the use of any of these other catalysts over CoCl_2 , since a specific rate of 0.02 min^{-1} was desired in this program. This general result would be expected from the preliminary studies of Schlesinger and his group⁽³⁾; they indicated that the actual catalysts were borides. The mechanism by which these boride catalysts are formed and operate, however, is not known and has not been studied in detail.

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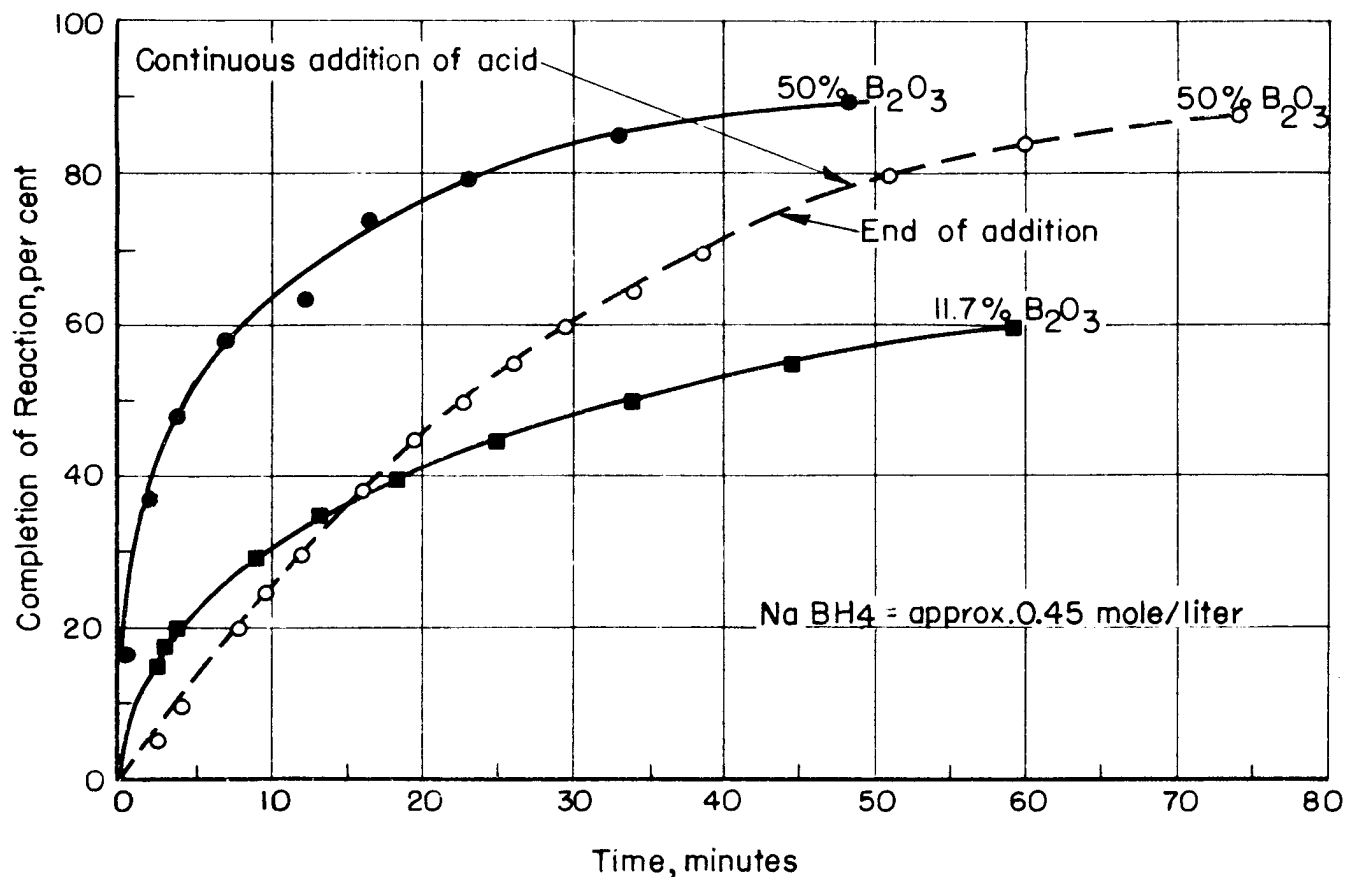


FIGURE 3. RATE CURVES FOR BORIC ACID-ACCELERATED HYDROLYSIS OF SODIUM BOROHYDRIDE

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TABLE 3. EFFECT OF FOUR CATALYSTS ON THE HYDROLYSIS OF SODIUM BOROHYDRIDE
 (Reaction conditions: solvent - 0.1M NaOH; catalysts
 added slowly; charge size - ca. 800 cc H₂)

Catalyst	Catalyst Concentration, mole/mole NaBH ₄	NaBH ₄ Concentration, mole/liter	Specific Rate, R _{sp} (50), min ⁻¹
NiCl ₂	0.0285	0.27	0.0032
NiCl ₂	0.0570	0.27	0.0071
NiCl ₂	0.0285	0.45	0.0033
CoCl ₂	0.0285	0.27	0.0346
CoCl ₂	0.0114	0.45	0.0194
CrCl ₃	0.0285	0.27	0.0011
CrCl ₃	0.0570	0.27	0.02 ⁽¹⁾
CrCl ₃	0.0285	0.45	0.011
AlCl ₃	0.0285	0.27	0.0013
AlCl ₃	0.0570	0.27	0.0031
AlCl ₃	0.0285	0.45	0.0017

(1) Possibly in error due to leak in system.

Note: The specific rate desired in this program is 0.02 min⁻¹.

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Method of Mixing Solutions

From a practical point of view, it would be desirable to add a minimum volume of CoCl_2 solution to the NaBH_4 solution. Since the literature referred to variations in results caused by the manner in which the reactants were introduced into the system, it was considered desirable to investigate the effects of mixing.

Figure 4 shows the results of several experiments conducted to establish the best method of mixing the solutions. There would be no advantage gained by the addition of the relatively large volume of borohydride solution to the relatively small volume of catalyst. Although Figure 4 does show variations in the rate of generation of hydrogen depending on the method of mixing, the general conclusion from these experiments is that it should be possible to add small volumes of CoCl_2 solution to the NaBH_4 solution so as to generate hydrogen at the rate desired.

It will be noted in Figure 4 that the CoCl_2 or the NaBH_4 solution was added in a continuous stream or dropwise. The rate of addition does have some effect on the rate of reaction, but this effect was of more consequence in these small-scale studies than it was found to be in larger scale experiments, described below.

The observations of Schlesinger⁽³⁾ and of Hoekstra⁽⁴⁾ concerning the appearance of the solution during the hydrolysis reaction have been borne out in the present study. When the two solutions are mixed, an insoluble black material is formed which is so finely divided that the solution appears to be homogeneous. The actual heterogeneity of the mixture at this stage is evident in the larger scale studies; from these, a truer over-all picture of the changes can be obtained. Schlesinger reports that this black

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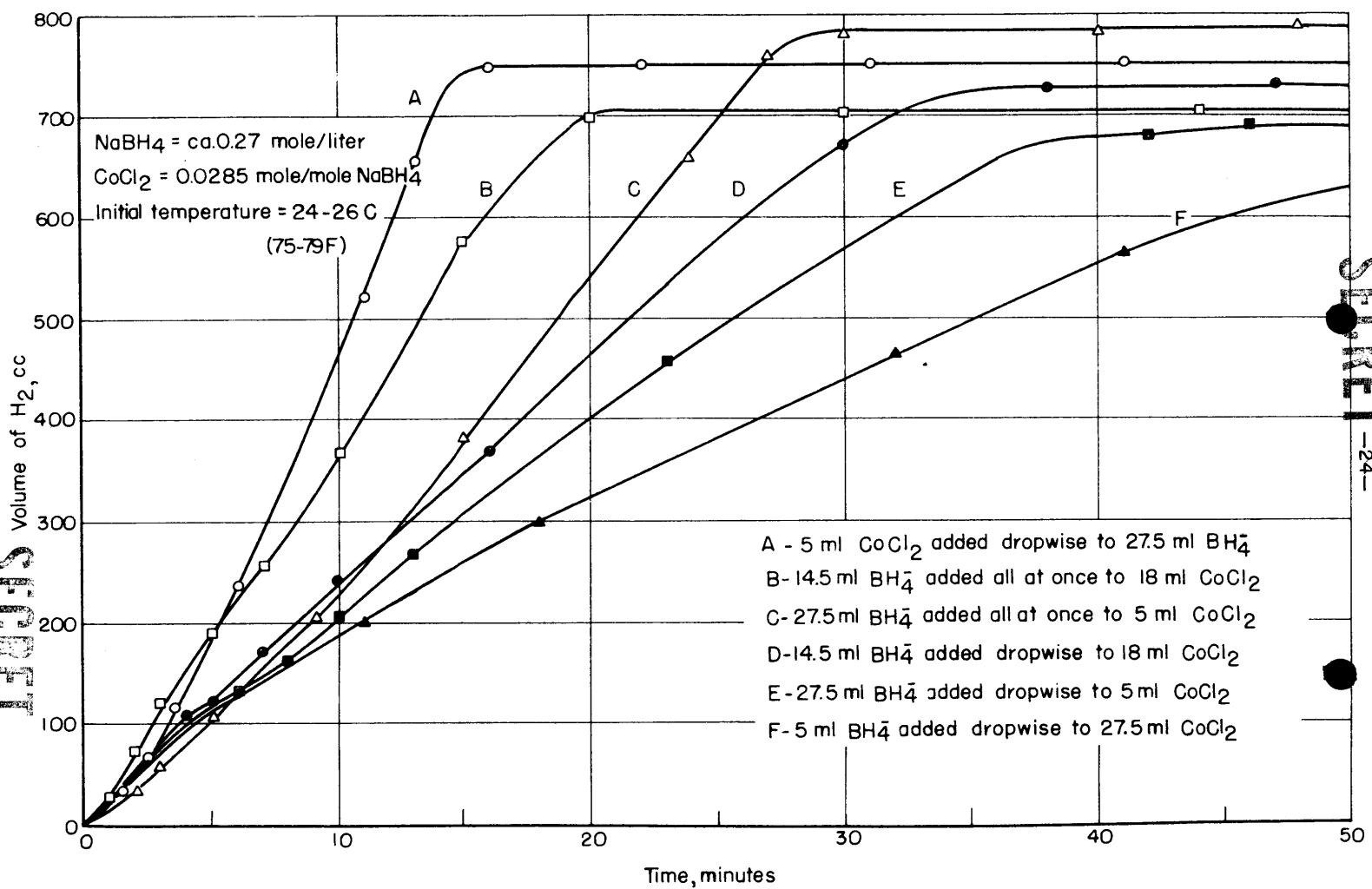


FIGURE 4. EFFECT OF METHOD OF MIXING ON HYDROLYSIS RATE (800-cc CHARGES)

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precipitate has a composition corresponding to the formula Co_2B . It is also stated that this material has about the same catalytic effect as is observed with fresh solutions of CoCl_2 . As will be discussed later, the findings of Schlesinger in this regard have been confirmed in the present study.

As a result of the experiments reported here, it can be concluded that the full-scale generator can be designed for the addition of the catalyst solution to the borohydride solution. Although it has been shown that for small charges (1 liter of hydrogen or less) the catalyst should be added dropwise, this procedure is not necessary for large-scale generation.

Solvent Effects

As shown in Figure 5, the hydrolysis reaction for NaBH_4 dissolved in a 0.1M NaOH solution proceeds differently from that for a borohydride - neutral water solution. The reaction in deionized water proceeds more rapidly initially, but does not accelerate as rapidly in the later stages of hydrolysis as does the reaction in the alkaline medium. This effect is probably related to the heat effects that occur as the metaborate-ion concentration increases during the reaction. It is possible that some tetraborate is also formed in the reaction, with an additional evolution of heat.

The study with the 0.1M NaOH solution was necessary because, in the operation of the full-size generator, it is probably preferable to dissolve the NaBH_4 in a basic solution, for two reasons. First, experience has shown that the borohydride is not so stable in neutral or even slightly alkaline solutions as has been implied by the literature. Second, natural waters may even be slightly acidic.

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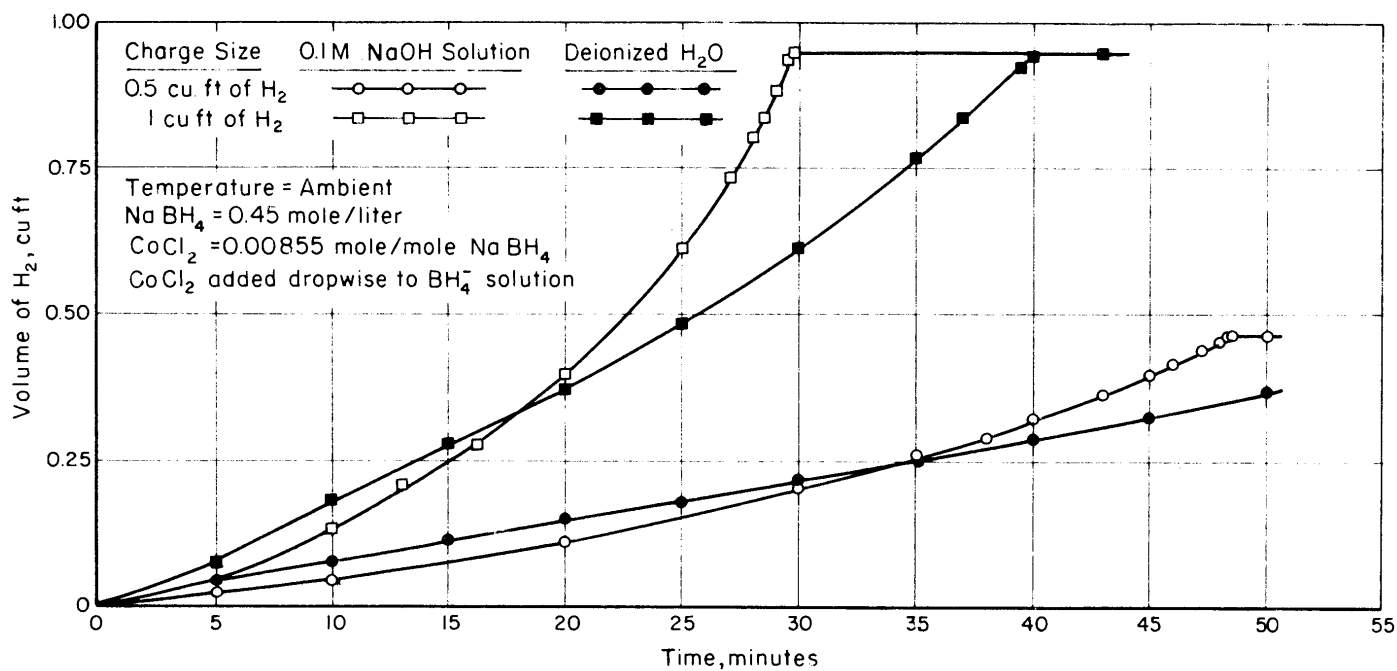


FIGURE 5. EFFECT OF SOLVENT ON RATE OF GENERATION

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The Effect of Borohydride and Catalyst
Concentrations on the Reaction

The amount of water present in a solution containing a fixed reaction charge of borohydride determines the adiabatic temperature rise caused by complete hydrolysis. The limiting temperature of the off-gas set by the specifications is 100 C (212 F); however, at this temperature the off-gas would be heavily laden with water vapor, and a means of drying the hydrogen would be necessary. It appeared desirable, therefore, to limit the allowable temperature rise.

NaBH_4 solutions at a concentration of 0.56 mole per liter were used arbitrarily in the preliminary experiments. Since the heat of reaction for the catalyzed hydrolysis is 57.5 kilocal per mole⁽³⁾, the calculated temperature rise occurring during hydrolysis of a solution with this borohydride concentration is 32.2 degrees C (58 degrees F). This temperature rise was considered to be reasonable and allowable in the proposed generator, and most of the subsequent research was done at this borohydride concentration level.

Figure 6 shows the effect of catalyst concentration on the generation rate for 1- and 2-cu-ft charges under isothermal conditions. The generation rates in Figure 6 are approximately proportional to the catalyst concentration.

Therefore, it is concluded that the generation rate and the temperature of the off-gas can be controlled, with a fair amount of latitude, by proper regulation of the catalyst and borohydride concentrations.

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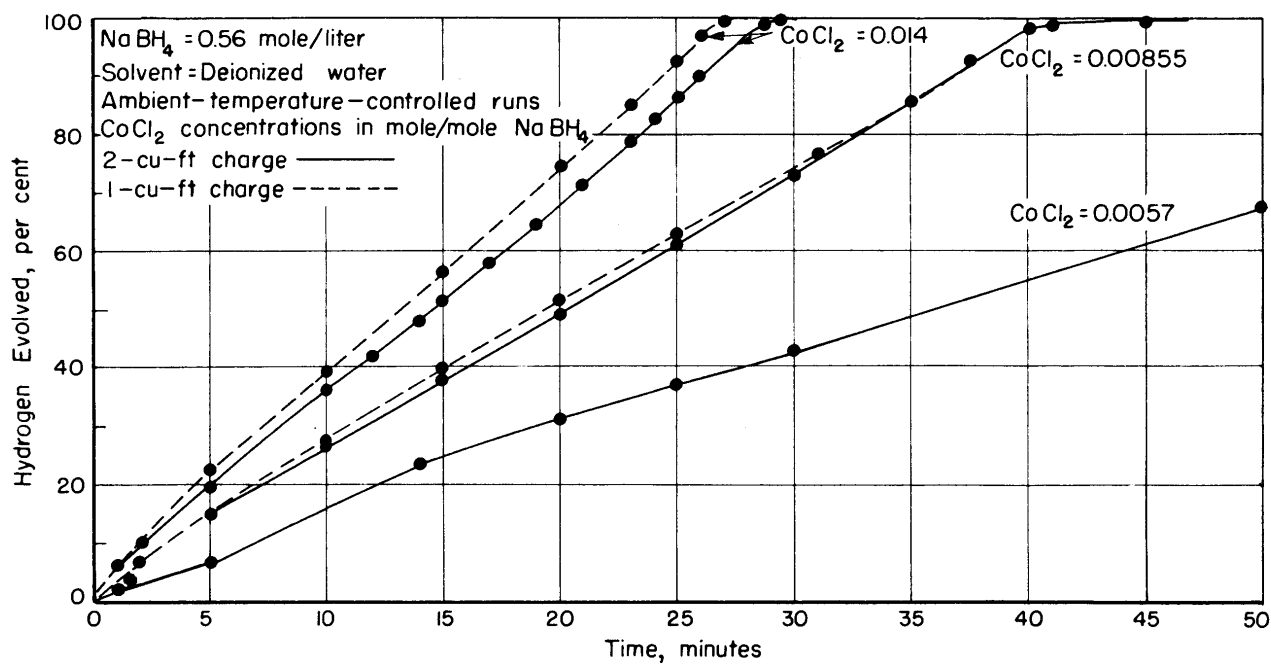


FIGURE 6. VARIATION OF GENERATION RATE WITH CATALYST CONCENTRATION

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The Effect of Scaling Factors on the Reaction SystemPreliminary Scaling Studies

A detailed study of the combined effect of charge size and catalyst concentration was made so that conditions for the full-scale generator could be extrapolated or predicted with assurance. If a completely adiabatic system or a system in which all of the heat losses can be taken into account is assumed, it should be possible to extrapolate from the conditions for generating hydrogen from any charge size to those for the full-scale generator. This assumes that the behavior of all of the variables is known and accounted for. The system of interest is concerned with a heterogeneous, catalyzed reaction. It is possible, therefore, that the distribution of the catalyst throughout the reacting medium may be a factor which does not scale readily. Consequently, preliminary scaling studies were conducted to determine the feasibility of scaling the $\text{CoCl}_2 - \text{NaBH}_4$ hydrolysis from small to relatively large charge sizes.

Tables 4, 5, and 6 summarize the scaling experiments for charges ranging in size from 0.5 to 3.5 cu ft of hydrogen. The reactions were run in the 1-gallon reactor. The principal variables were charge size (in almost all of the experiments, the borohydride concentration was 0.56 mole/liter) and catalyst concentration. The data were analyzed with respect to the 50-min specific rate, $R_{sp(50)}$, solution temperatures, and foam volume.

The general conclusions drawn from the data in these three tables are that scaling is independent of the charge size, i.e., the specific rate is independent of the charge size; but that the specific rate increases as

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TABLE 4. DATA FROM SCALING EXPERIMENTS IN THE ONE-GALLON REACTOR WITHOUT TEMPERATURE CONTROL

(Reaction conditions: NaBH_4 - 0.56 mole/liter;
solvent - deionized water; CoCl_2 added all at
once; no temperature control)

Charge Size, cu ft of H ₂	CoCl ₂ Concen- tration, mole/ mole NaBH ₄	Specific Rate ⁽¹⁾ , R _{sp} (50), min ⁻¹	Temperature				Foam Vol- ume, ml
			Initial		Maximum		
			C	F	C	F	
0.518	0.00570	0.0127	23	73	32	90	5
1.05	0.00570	0.0158	23	73	43	109	10
1.56	0.00570	0.0097	20	68	37	99	50
2.09	0.00570	0.0145	22	72	46	115	275
0.522	0.00855	0.0216	24	75	39	102	20
1.05	0.00855	0.0298	24	75	46	115	100
1.56	0.00855	0.0277	23	73	47	117	300
2.09	0.00855	0.0332	25	77	50	122	375
3.52	0.00855	0.0316	26	79	53	127	1,000
0.524	0.01140	0.0369	23	73	42	108	10
1.05	0.01140	0.0399	23	73	47	117	125
1.57	0.01140	0.0431	24	75	51	124	410
2.09	0.01140	0.0312	24	75	50	122	375
3.44	0.01140	0.0345	26	79	52	126	650

(1) The specific rate of 0.02 min^{-1} is desired for the proposed generator.

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TABLE 5. DATA FROM SCALING EXPERIMENTS IN THE ONE-GALLON REACTOR AT CONSTANT TEMPERATURE

(Reaction conditions: NaBH_4 - 0.56 mole/liter;
solvent - deionized water; CoCl_2 added all at
once; temperature controlled with water bath)

Charge Size, cu ft of H ₂	CoCl ₂ Concen- tration, mole/ mole NaBH ₄	Specific Rate ⁽¹⁾ , R _{sp} (50), min ⁻¹	Temperature				Foam Vol- ume, ml
			Initial		Maximum		
			C	F	C	F	
0.522	0.0057	0.0124	27	81	28	82	0
1.04	0.0057	0.0085	23	73	24	75	0
1.56	0.0057	0.0113	25	77	28	82	25
2.09	0.0057	0.0134	26	79	30	86	50
3.51	0.0057	0.0063	20	68	21	70	25
0.526	0.00855	0.0152	27	81	29	84	5
1.05	0.00855	0.0239	26	79	33	91	10
1.56	0.00855	0.0172	26	79	31	88	100
2.08	0.00855	0.0243	27	81	36	97	100
3.51	0.00855	0.0185	25	77	32	90	275
0.524	0.0114	0.0246	26	79	30	86	25
1.05	0.0114	0.0368	27	81	35	95	75
1.56	0.0114	0.0249	25	77	32	90	50
2.09	0.0114	0.0346	25	77	36	97	300
3.51	0.0114	0.0283	25	77	36	97	350

(1) The specific rate of 0.02 min^{-1} is desired for the proposed generator.

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TABLE 6. DATA FROM SCALING EXPERIMENTS IN THE ONE-GALLON REACTOR USING ALKALINE SOLUTION

(Reaction conditions: solvent 0.1M NaOH;
CoCl₂ added dropwise; no temperature control)

Charge Size, cu ft of H ₂	NaBH ₄ Concentration, mole/liter	CoCl ₂ Concentration, mole/mole NaBH ₄	Specific Rate ⁽¹⁾ , R _{sp} (50), min ⁻¹	Temperature				Foam Volume, ml
				Initial C	Maximum F	Initial C	Maximum F	
1.05	0.56	0.0057	0.0029	27	81	30	86	0
2.09	0.56	0.0057	0.0232	29	84	55	131	650
2.09	0.56	0.00855	0.0392	27	81	54	129	1,000
1.05	0.53	0.00855	0.0340	28	82	51	124	275
0.52	0.45	0.00855	0.0202	28	82	42	108	70
0.52	0.45	0.00855	0.0142	23	73	35	95	0
1.05	0.45	0.00855	0.0298	28	82	47	117	200
1.04	0.45	0.00855	0.0248	23	73	41	106	50
2.09	0.45	0.00855	0.0397	28	82	51	124	650
0.52	0.56	0.0114	0.0455	26	79	47	117	150
1.05	0.56	0.0114	0.0277	25	77	47	117	400
1.05 ⁽²⁾	0.56	0.0114	0.0325	23	73	46	115	300
1.08	0.56	0.0114	~0.024	29	84	53	127	375
1.57	0.56	0.0114	0.0643	27	81	54	129	900
2.09	0.56	0.0114	0.0870	27	81	56	133	1,700

(1) The specific rate of 0.02 min⁻¹ is desired for the proposed generator.(2) CoCl₂ added all at once.**SECRET**

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the CoCl_2 concentration is increased, all other variables being held substantially constant. Table 4, for example, shows that the specific rate is 0.010 to 0.016 min^{-1} in the runs with a CoCl_2 concentration of 0.0057 mole per mole NaBH_4 , 0.022 to 0.033 min^{-1} for a CoCl_2 concentration of 0.00855 mole per mole NaBH_4 , and 0.031 to 0.043 min^{-1} for a CoCl_2 concentration of 0.0114 mole per mole NaBH_4 . It was apparent, however, that this range in the specific rate for each CoCl_2 concentration level is at least partially due to a variation in the initial temperatures.

The foam-volume data are of interest because in the Ethyl study⁽²⁾ large volumes of foam were produced at high rates of hydrogen generation. It was feared that large volumes of foam would be a major problem in the Task Order No. C program. For this reason, these data were collected along with the specific-rate and temperature-rise data. From Tables 4, 5, and 6, it is obvious that the foam volume generally increases as the specific rate increases, and also as the charge size increases. The increase of foam volume with specific rate is to be expected. The increase of foam volume with charge size might not be expected. With regard to this point, however, it will be recalled that these reactions were run in a reactor of constant diameter. As a result, the charge size varied with the depth of solution. Consequently, at any particular specific rate, the amount of hydrogen passing off the surface of the solution increased as the charge size was increased. Therefore, in these experiments, the foam volume increased with charge size because more hydrogen was released from the solution as the depth of the solution, i.e., as the charge size, was increased.

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The results of these preliminary experiments indicate that foaming is not a major problem, since the foam volumes were relatively small. This conclusion was confirmed in the large-scale studies.

The general conclusions drawn from the preliminary scaling study are as follows:

- (1) The $\text{CoCl}_2\text{-NaBH}_4$ hydrolysis reaction lends itself to scaling.
- (2) The reaction is rather sensitive to the initial temperature of the water.
- (3) There is an increasing volume of foam as the charge size increases; this is related to the solution height as well as to the specific rate.

Large-Scale Studies

The purpose of the large-scale studies was to confirm the results of the previous preliminary studies, and also to establish the design parameters for the full-scale generator. The large-scale studies, which may also be referred to as aliquot-scaling studies, are based upon three premises:

- (1) That the concentration of NaBH_4 in the full-scale reactor will be 0.56 mole per liter.
- (2) That the general shape of the reaction pool in the full-scale generator will be approximately that of a pool 1.5 ft in depth and 50 sq ft in surface area.
- (3) That the reaction system in this pool approximates an adiabatic system.

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On the basis of these premises, the full-scale generator can be considered to consist of a summation of a number of small generators, each 1.5 ft deep and evolving hydrogen in proportion to the surface area of the solution. In an "aliquot" of the full-scale-generator pool, an aliquot amount of hydrogen should be generated at the same rate as would be the case in the full-scale pool. Naturally, this reasoning is valid only when the thermal conditions for the reaction in the experimental aliquot reactor approach those in the full-scale pool.

Tables 7 and 8 summarize the results of the aliquot-scaling studies. The data in each of these tables are grouped in sections of constant CoCl_2 concentration, and each section shows the effect of charge size on specific rate, temperature rise, and foam height under the conditions of the experiments. The column titled "Surroundings" refers to whether the hydrolysis proceeded at ambient temperature; with an attempt to control the temperature by means of insulation; or as a temperature-controlled experiment in a water bath. The last column in Table 7 indicates the time for complete reaction for some of the experiments. These times are of interest because, in many instances, specific-rate values fail to give an adequate description of the shape of the generation-rate curve. In the first run listed in Table 7, for example, the reaction was less than 50 per cent complete in 50 min, but was 100 per cent complete in 77 min.

The results in Tables 7 and 8 for the large-scale experiments are generally similar to those presented previously for the small-scale studies. The data show that (1) the specific rate increases with catalyst concentration, (2) the initial temperature has an appreciable effect on the specific rate,

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TABLE 7. DATA FROM LARGE-SCALE STUDIES WITH DEIONIZED-WATER SOLUTIONS
(Reaction conditions: NaBH_4 - 0.56 mole/liter; CoCl_2 added
all at once)

Charge Size, cu ft of H ₂	CoCl ₂ Concen- tration, mole/ mole NaBH ₄	Specific Rate, R _{sp} (50), min ⁻¹	Temperature				Foam Height, in.	Surroundings ⁽¹⁾	Time for Com- plete Reaction, min
			Initial		Maximum				
			C	F	C	F			
36.4	0.0057	0.0087	24.1	75.4	52.6	127	2-3/4	Ambient	77
1.4	0.00855	0.0097	24.4	75.9	34	93	1-1/2	Ambient	-
3.1	0.00855	0.0080	19.4	66.9	35	95	1-1/2	Ambient	-
11.4	0.00855	0.0116	25.6	78.1	45.4	114	1-1/2	Ambient	-
36.4 ⁽²⁾	0.00855	0.0183	24.1	75.4	52.7	127	3-1/2	Ambient	52
36.4 ⁽²⁾	0.00855	0.0156	22.7	72.9	52.2	126	5-1/4	5" of vermiculite	56
1.4	0.00855	0.0061	24	75.2	25	77	<1	W.B. 20.3 C (68.5 F)	-
3.1	0.00855	0.0070	20.6	69.1	22	71.6	1/4	W.B. 20.6 C (69.1 F)	-
1.4	0.0114	0.0142	25	77	39	102	2-1/2	Ambient	-
3.1	0.0114	0.0195	25	77	45.5	114	3-3/4	Ambient	-
11.4	0.0114	0.0116	23.0	73.4	46.8	116	2	Ambient	87
11.4	0.0114	0.0169	25.4	77.7	53.6	128	1-1/2	5" of vermiculite	61

TABLE 7 (Continued)

Charge Size, cu ft of H ₂	CoCl ₂ Concen- tration, mole/ mole NaBH ₄	Specific Rate, R _{sp} (50), min ⁻¹	Temperature				Foam Height, in.	Surroundings ⁽¹⁾	Time for Com- plete Reaction, min
			Initial		Maximum				
			C	F	C	F			
36.4	0.0114	0.0278	25.4	77.7	54.0	129	2-1/2	Ambient	-
1.4	0.0114	0.0078	23.3	73.9	25	77	1-1/4	W.B. 22.5 C (72.5 F)	-
3.1	0.0114	0.0080	20.6	69.1	22.9	73.2	1/2	W.B. 20 C (68 F)	-
1.4	0.0171	0.0179	24.1	75.4	39.5	103	3-1/2	Ambient	-
3.1	0.0171	0.0174	22.4	72.3	-	-	3-1/4	Ambient	-
11.4	0.0171	0.0179	24.2	75.6	48.3	119	2	Ambient	65
1.4	0.0171	0.0123	24	75.2	26.5	79.7	1-1/2	W.B. 20.4 C (68.7 F)	-
3.1	0.0171	0.0103	18.9	66.0	21.7	71.1	1	W.B. 18.5 C (65.3 F)	-
11.4	0.0228	0.0197	23.0	73.4	47.0	117	5-1/2	Ambient	-

(1) W.B. = water bath.

(2) See Figure 8 for plot of temperature rise versus per cent reaction.

TABLE 8. DATA FROM LARGE-SCALE STUDIES WITH ALKALINE SOLUTIONS

(Reaction Conditions: NaBH_4 - 0.56 mole/liter;
0.1 M NaOH solution; CoCl_2 added all at once)

Charge Size, cu ft of H ₂	CoCl ₂ Concen- tration, mole/ mole NaBH ₄	Specific Rate, R _{sp} (50), min ⁻¹	Temperature				Foam Height, in.	Surroundings ⁽¹⁾
			Initial		Maximum			
			C	F	C	F		
1.4	0.00855	0.0057	22.9	73.2	29.5	85.1	1-1/4	Ambient
3.1	0.00855	0.0163	~ 24.5 ~ 76.1		-	-	5-1/2	Ambient
11.4	0.00855	0.0061	23.2	73.8	47.4	117	1-1/2	Ambient
36.4	0.00855	0.0207	24.6	76.3	53.4	128	4-1/2	Ambient
1.4	0.00855	0.0054	24.2	75.6	25.4	77.7	1/2	W.B. 24.5 C (76.1 F)
3.1	0.00855	0.0088	24.0	75.2	26.4	79.5	1	W.B. 24 C (75.2 F)
1.4	0.0114	0.0076	23.9	75.0	31.0	87.8	1	Ambient
3.1	0.0114	0.0131	24.0	75.2	39.6	103	2-1/2	Ambient
11.4 ⁽²⁾	0.0114	0.0131	23.9	75.0	43.3	110	1-1/4	Ambient
1.4	0.0114	0.0095	24.4	75.9	26.1	79.0	1-3/4	W.B. 24.2 C (75.6 F)
3.1	0.0114	0.0105	24.1	75.4	27.0	80.6	1-3/4	W.B. 24.1 C (75.4 F)
1.4	0.0171	0.0157	25.3	77.5	41.0	106	3-1/4	Ambient
3.1	0.0171	0.0152	24.6	76.3	39.8	104	3-1/2	Ambient

TABLE 8 (Continued)

Charge Size, cu ft of H ₂	CoCl ₂ Concen- tration, mole/ mole NaBH ₄	Specific Rate, R _{sp} (50), min ⁻¹	Temperature				Foam Height, in.	Surroundings ⁽¹⁾
			Initial		Maximum			
			C	F	C	F		
11.4	0.0171	0.0200	25.1	77.2	48.4	119	3-3/4	Ambient
1.4	0.0171	0.0131	24.2	75.6	25.6	78.1	2-1/4	W.B. 24.0 C (75.2 F)
3.1	0.0171	0.0127	24.0	75.2	26.2	79.2	1-3/4	W.B. 24.0 C (75.2 F)

(1) W.B. = water bath.

(2) Catalyst volume to borohydride volume = 1:75.

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and (3) the NaOH-NaBH_4 solutions reach complete reaction sooner than do de-ionised-water solutions, particularly in the 11.4 and 36.4-cu-ft reactors.

Two runs in Table 7 in which the reactor was insulated with a 5-in.-thick wall of vermiculite are of special interest. The results for these two runs, when compared with those for noninsulated runs of the same charge sizes, show that the 36.4-cu-ft reactor approaches the desired "adiabatic" reactor. The temperature rises in the 11.4-cu-ft experiments were 28.2 and 23.8 degrees C, respectively, and those in the 36.4-cu-ft experiments were 29.5 and 28.6 degrees C, respectively, for the insulated and noninsulated runs. These temperature-rise data show that the 11.4-cu-ft reactor still loses an appreciable amount of heat to its surroundings, while the 36.4-cu-ft reactor loses only a small amount to its surroundings, as compared to the amount of heat which is retained in the reacting solution. In addition, the temperature rises in the larger reactor more nearly approach that expected on the basis of theoretical considerations.

Figure 7 illustrates this "approach to adiabatic conditions" with increasing charge size. The lower initial temperatures for the 3.1- and 36.4 (insulated)-cu-ft runs explain why the two curves appear "out of order" in Figure 7. The specific rate generally increased with charge size, as shown in Figure 7 and Tables 7 and 8, because of this "approach to adiabatic conditions".

Figure 8 shows the variation between the theoretical and observed temperature rises in two 36.4-cu-ft runs (see Table 7). The theoretical curve is based on 57.5 kilocal per mole for the heat of reaction and 0.56 mole NaBH_4 per liter for the solution concentration. There was close agreement between the two experimental curves, B and C; the noninsulated reaction

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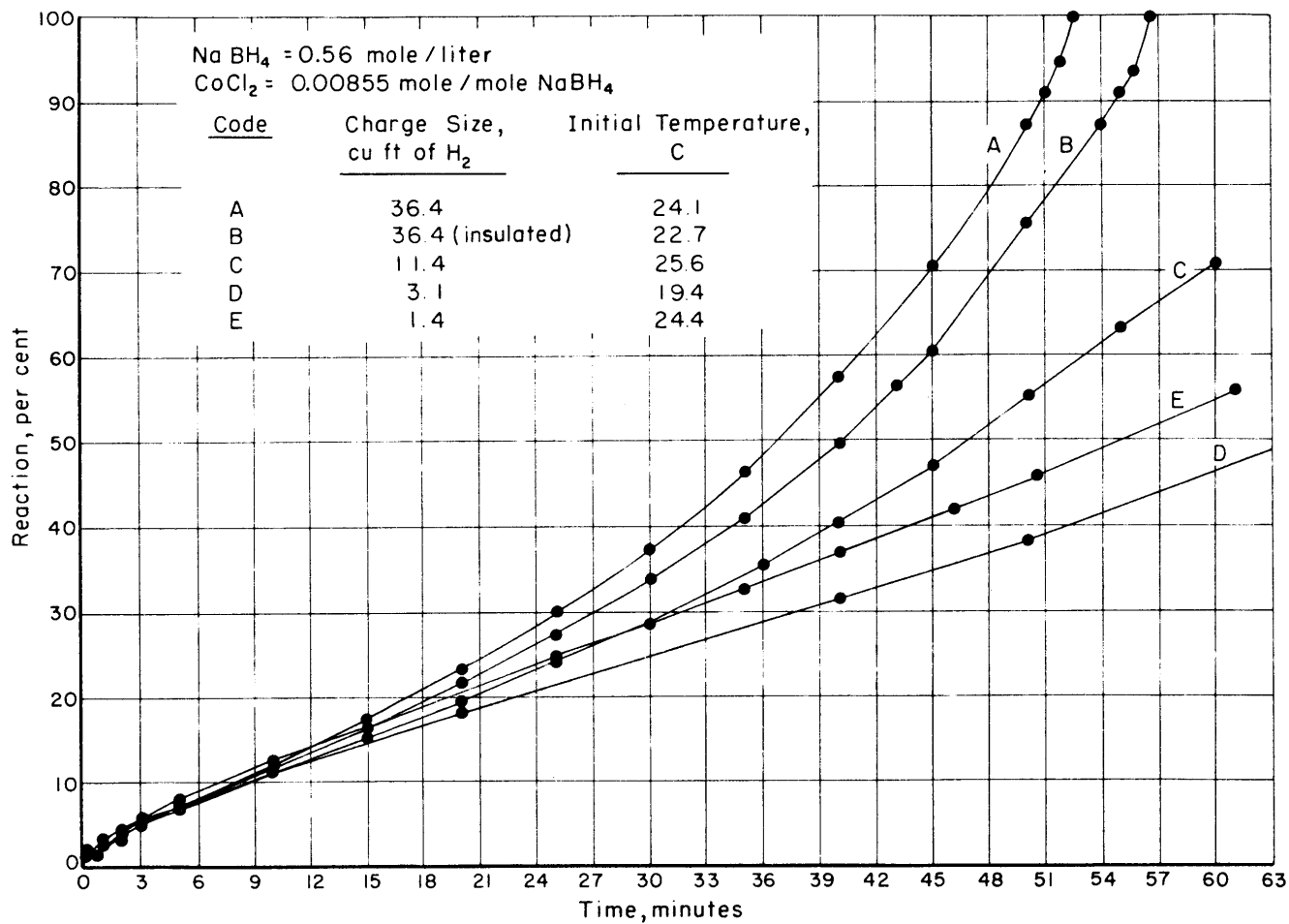


FIGURE 7. THE VARIATION OF GENERATION RATES WITH CHARGE SIZE

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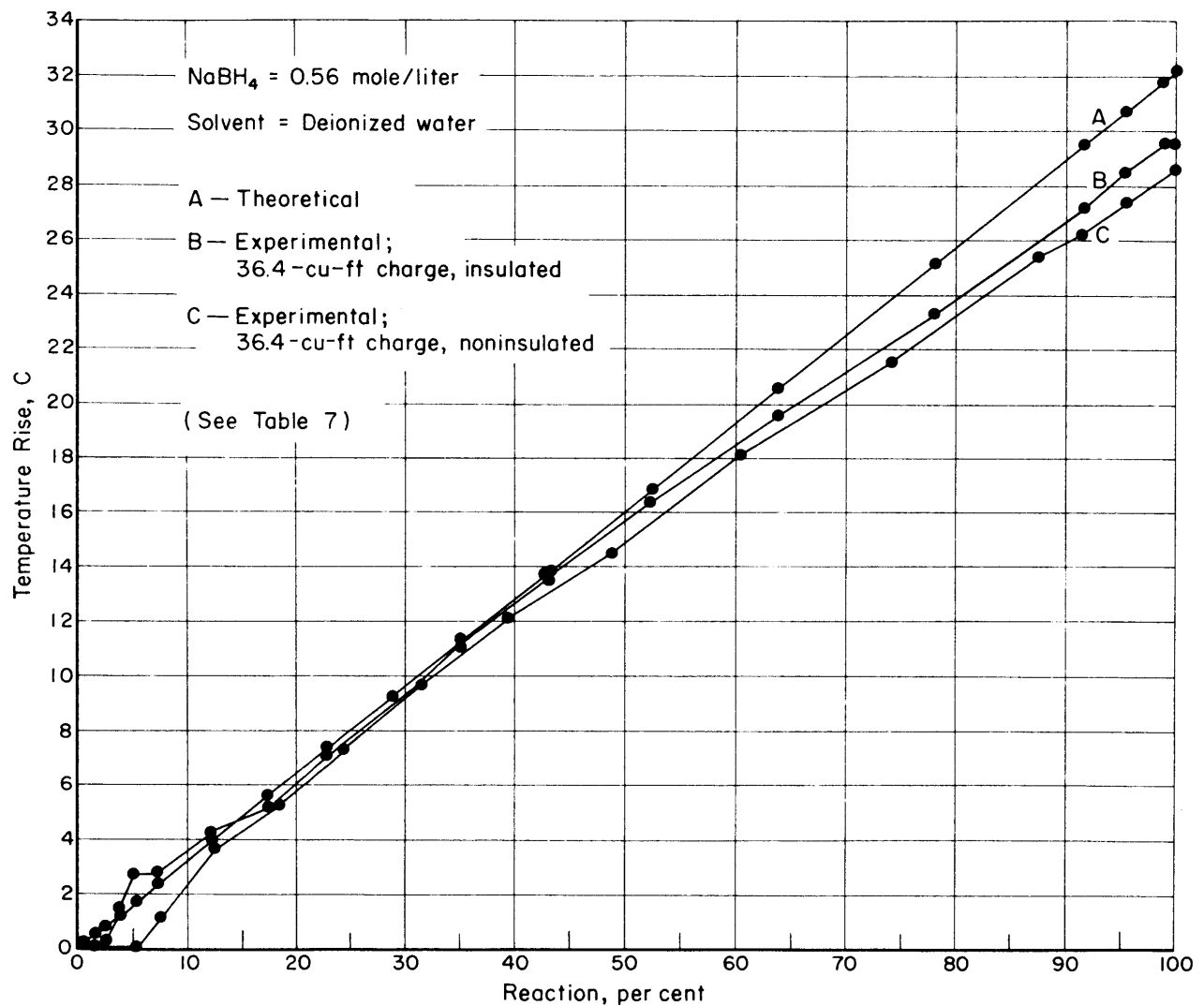


FIGURE 8. THEORETICAL AND EXPERIMENTAL TEMPERATURE RISES

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system was only about 3 per cent "less adiabatic" than the insulated reaction system. Up to about 60 per cent reaction, the temperature rises in the experimental systems agreed within about 5 per cent with the theoretical temperature rise. The insulated system was not completely adiabatic, as is apparent in Figure 8. A thermocouple set in the vermiculite about 1.5 in. from the reactor wall showed a temperature rise of 6 degrees C (11 degrees F) during the course of this run.

On the basis of the results shown in Figures 7 and 8, it is evident that conditions established on the basis of reactions in the 36.4-cu-ft reactor approach those to be expected in the full-scale generator. In view of the temperature-rise data of Figure 8, it is estimated that the generation rates in this reactor are probably about 90 per cent of those obtainable in a completely adiabatic reactor.

Based on these analyses, it is believed that the following conditions are probably necessary in order to effect complete generation of large amounts of hydrogen from alkaline (0.1 M NaOH) or deionized-water solutions of NaBH_4 in about 50 min:

NaBH_4 concentration - 0.56 mole/liter

CoCl_2 concentration - 0.00855 mole/mole NaBH_4

Initial temperature - 22 to 23 C (72 to 73 F).

The Effect of Water Contaminants on the Reaction

There does not appear to be any major problem in generating hydrogen under conditions involving almost any rate, temperature rise, and foam

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volume when the solvent is deionized water or a NaOH solution. However, the specified requirements for the proposed generator indicate that only natural waters, such as those from a lake, pond, or flowing stream, will be available at the operating site. For this reason, it was considered necessary to investigate the hydrolysis of NaBH_4 in natural waters and to determine the effects of these waters on the reaction.

The study with natural-type waters was divided into three parts. The study was initially directed toward obtaining specific-rate data for the hydrolysis at various CoCl_2 concentrations using deionized water, tap water, and water from the . When it was found that there was a decrease in specific rates when river waters were used as the solvent, it was decided to investigate this decrease in more detail. This portion of the study was conducted by first checking into the most prevalent minerals which could occur in natural waters and then studying the effects of these minerals added to deionized water. Finally, the effect of organic matter was investigated briefly.

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Type of Water

The water-type experiments were conducted in a 3.2-in.-diameter reactor (charge size of 4.1 cu ft of hydrogen), similar to the cylindrical reactors used in the previously described large-scale studies, at a NaBH_4 concentration of 0.56 mole per liter. A few runs were also made with 11.4- and 36.4-cu-ft charges.

Table 9 summarizes the specific rates obtained from the natural-water study as a function of both charge size and catalyst concentration.

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TABLE 9. DATA ON THE EFFECT OF NATURAL WATERS ON THE SPECIFIC RATE
(Reaction conditions: NaBH_4 0.56 mole/liter)

CoCl ₂ Concentration, mole/ mole NaBH_4	Specific Rate, $R_{sp}(50)$, minute ⁻¹						
	4.1-cu-ft Charge			11.4-cu-ft Charge		36.4-cu-ft Charge	
	Deionized Water	Tap Water		Deionized Water		Deionized Water	
0.0114	0.0130	-	0.0087 0.0074 0.0086	0.0116 (87) [23.0 C]	0.0082 (70) [24.2 C]	0.0278 [25.4 C]	0.0136 (63) [24.1 C]
0.0171	0.0197 0.0166 0.0178 0.0173	0.0161 0.0163	0.0117 0.0139	0.0178 (65) [24.2 C]	0.0191 (54) [23.2 C]	-	0.0184 (56) 0.0247*
0.0228	0.0198	0.0196 0.0192	0.0181 (72) 0.0182 0.0134* 0.0200*	0.0197 [23.0 C]	0.0194 (60) [24.4 C]	-	0.024
0.0285	-	-	0.0199	-	-	-	-

Notes: 1. Numbers in parentheses refer to time for complete reaction in minutes.
2. Numbers in brackets refer to initial solution temperature; otherwise, the initial temperature was ambient.

*0.01N NaOH solution.

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The general conclusion from the water-type study is that natural river waters affect the hydrolysis reaction only slightly. The runs in the 4.1-cu-ft reactor indicated that the reactions with deionized water proceeded more rapidly than those with river or tap water. The runs in the 11.4- and 36.4-cu-ft reactors, however, showed that the reduction in specific rate when natural waters were used was less than was indicated by the 4.1-cu-ft-reactor data. This decrease in the reduction in specific rate is attributable to the fact that the larger reactors lose less heat to the surroundings; as a result, the accelerated generation that occurs in the later stages of the reaction cancels out some of the specific-rate-reduction effect of the solvent.

A value for the difference between specific rates obtained with deionized and with natural waters cannot be arrived at with any degree of certainty. However, based on the 11.4- and 36.4-cu-ft-charge data of Table 9, it is estimated that the use of natural waters instead of deionized water reduced the specific rate by about 20 per cent. It is emphasized that, in connection with the interpretation of these data, consideration should be given to the initial temperature of the reaction.

Effect of Individual Minerals

In the second part of the water-type study, an attempt was made to determine which impurities in natural waters were causing the reduced specific rates. Table 10 shows the average composition of North American waters as indicated by Reference 6. The salinity, usually expressed as parts per million (ppm) of total dissolved solids, is reported to vary from 16 to

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TABLE 10. COMPOSITION OF NORTH AMERICAN WATERS⁽⁶⁾

Substance	Total Dissolved Solids, ppm		
	Minimum	Average	Maximum
CO ₃	0.01	33.40	65.6
SO ₄	0.00	15.31	66.4
Cl	0.68	7.44	46.4
NO ₃	0.07	1.15	4.1
Ca	0.00	19.36	30.5
Mg	0.18	4.87	15.4
Na	0.45	7.46	41.3
K	-	1.77	4.5
(Fe,Al) ₂ O ₃	0.00	0.64	6.6
SiO ₂	0.01	8.60	42.4

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227,200 ppm; the average for natural waters usually ranges from 100 to 500 ppm. There was little information in the literature on specific organic impurities that might be found in natural waters. It is to be expected that vegetation decomposition may produce organic acids which would reduce the pH of natural waters to a value of 5 or even lower, while photosynthetic action in relatively hard waters might raise the pH to values above 8.

The impurities listed in Table 10 were added individually to deionized-water solutions of NaBH_4 , and specific-rate data, temperature-rise data, and maximum foam heights were determined. Table 11 summarizes the results of these experiments. The column titled "Foam Height" shows two values for most of the additives. In those cases, a foam formed as soon as the CoCl_2 was added. This foam decreased in height fairly rapidly, and then more foam was produced later in the reaction. Of the two values indicated, the first refers to the initial foam, and the second to the later or regular foam. For purposes of comparison, the first four runs listed in Table 11 show the specific-rate data for normal solutions, i.e., for NaBH_4 dissolved in deionized water.

With the exception of sodium silicate, the impurities evaluated did not cause any appreciable change in the specific rate. The sodium silicate had a very marked and interesting effect in that it caused an increase rather than a decrease in specific rate. It is probable that the increased specific rate is due to the formation of a more active or more finely divided catalyst in the presence of the silicate. A second run was made with the sodium silicate to confirm that the effect was real, and confirmation

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TABLE 11. DATA ON THE EFFECT OF VARIOUS MINERALS ON THE HYDROLYSIS RATE
(Reaction conditions: NaBH_4 - 0.56 mole/liter of deionised-
water solution; CoCl_2 - 0.0171 mole/mole NaBH_4 ; charge size -
4.1 cu ft)

Additive		Specific Rate, R _{sp} (50), min ⁻¹	Temperature				Foam Height*, in.
Name	Wt, g		Initial		Maximum		
			C	F	C	F	
-	-	0.0166	25.2	77.4	43.5	110	2
-	-	0.0178	24.2	75.6	44.7	112	4
-	-	0.0173	25.6	78.1	43.3	110	2-1/2
-	-	0.0185	24.4	75.9	42.8	109	4
Calcium chloride	0.331	0.0198	25.4	77.7	46.8	116	6, 2-1/4
Potassium chloride	0.437	0.0164	24.2	75.6	42.6	109	3, 1-1/2
Ferrous chloride (.4H ₂ O)	1.03	0.0170	24.0	75.2	40.8	105	3, 2
Aluminum chloride (.6H ₂ O)	2.74	0.017	25.8	78.5	43.3	110	5, 6
Magnesium chloride (.6H ₂ O)	0.225	0.0157	24.4	75.9	40.6	105	2-1/2, 1
Sodium hexametaphosphate (Calgon)	0.450	0.0156	24.4	75.9	40.8	105	1-1/2
Sodium carbonate	5.43	0.0180	24.5	76.1	41.3	106	1-1/2
Sodium nitrate	0.332	0.0151	24.0	75.2	37.4	99.3	3, 2
Sodium nitrate	0.665	0.0178	24.3	75.8	43.3	110	3, 1
Sodium chromate (.4H ₂ O)	0.229	0.0156	25.1	77.2	42.8	109	3, 1-1/2
Sodium sulphate	4.57	0.0181	24.9	76.9	42.2	108	3-1/2
Sodium silicate (.9H ₂ O)	10.36	>0.034	24.2	75.6	47.1	117	5
Sodium silicate (.9H ₂ O)	10.36	0.0256	24.6	76.3	45.8	114	3, 2
Tannic acid	0.752	0.0166	25.2	77.4	43.5	110	3, 1

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TABLE 11 (Continued)

Additive		Specific Rate, $R_{sp}(50),$ min^{-1}	Temperature				Foam Height*, in.
Name	Wt, g		<u>Initial</u>		<u>Maximum</u>		
			C	F	C	F	
Mixture of:		0.0173	24.1	75.4	44.4	112	2-1/4; 1-3/4
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	0.499						
NaNO_3	0.405						
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	4.00						
KCl	0.204						
CaCl_2	0.207						
	5.315						

*When two values are given, the first refers to the initial foam that formed when the CoCl_2 was added, and the second, to the foam that formed later.

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was obtained. The effect of the sodium silicate addition was not pursued further.

The Effect of Organic Matter

Since the literature did not indicate any specific organic impurities in natural water for consideration here, it was felt advisable to evaluate the effect of a stagnant type of water. Five samples of stagnant waters were obtained from various locations in the vicinity of and these were tested with NaBH_4 . Hydrolysis occurred in all five of the water samples as soon as the borohydride was added.

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A quantitative check of one stagnant water sample showed approximately 18 per cent hydrolysis in 24 min. Sodium borohydride was dissolved in a second sample of the same water which had previously been made basic (0.1M NaOH); there was no evolution of hydrogen in 30 min. This experiment bears out the value of adding a base to the water used, before dissolving the NaBH_4 . Such an addition will not guarantee the stability of a NaBH_4 solution, but, as a precautionary measure, it will at least neutralize to some extent any acidic properties of a natural water.

The general conclusions drawn from the natural-water investigations are that: (1) local river waters cause about a 20 per cent decrease in specific rate, and (2) stagnant (swamp-like) waters are "active" and require the addition of a base to neutralize them, so that the borohydride solution prepared will be relatively stable.

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The Effect of Temperature on the Rate of Hydrolysis

The importance of temperature in the hydrolysis reaction has been brought out qualitatively at various points in the preceding discussion. It is of significance, however, to be able to make some quantitative approximations of the effect of temperature on this reaction. The literature contains very little information on the reaction kinetics of the catalyzed hydrolysis of NaBH_4 . It was necessary, therefore, to study some of the kinetic parameters of this reaction.

Experimental Procedure

There are some differences between the previously described experimental procedures and those used in the study on the temperature effect, and these warrant discussion here. These temperature-dependency experiments were run on small charges (500 cc to 1 liter of hydrogen) in a 50-ml reaction flask, and the hydrogen was collected over water in a gas burette, as previously described.

Only 25 ml of solution was used in each experiment; 5 ml of CoCl_2 solution was added to 20 ml of borohydride solution. If this reaction involved a homogeneous catalysis rather than a heterogeneous catalysis, this ratio of solution volumes used would be of no importance. However, since the reaction is heterogeneously catalyzed, the ratio of the volumes of catalyst solution to borohydride solution, and the general reactor geometry, affect the distribution of the catalyst when the two solutions are mixed. Ideally, uniform catalyst distribution is desired throughout the reacting system; in the full-scale unit, this will be a problem. For this study of the kinetics of

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the reaction only, the ratio of the solution used was 1:4 so that the catalyst would be relatively uniformly dispersed and, therefore, the factor of nonuniform dispersion would not affect the results. It will be recalled that in the scaling studies a ratio of 1:30 was used, because of the desirability of keeping the catalyst solution to a relatively small volume in connection with the ultimate full-scale generator.

It should also be pointed out that there was no stirring action in these experiments, except for that due to the evolution of hydrogen. In a precise kinetic study of a heterogeneous reaction, uniform stirring should be maintained; however, since the large-scale generator is also stirred only by the evolution of gas, the same stirring action was allowed to prevail in these experiments. As will be apparent in the following discussion, some of the scatter in the kinetic data, as well as some of the anomalous results, may be related to aspects of this experimental procedure.

Experimental Results

Rate experiments were performed at four temperatures - 20, 25, 30, and 35 C (68, 77, 86, and 95 F) - and at three NaBH_4 concentrations - 0.13, 0.26, and 0.56 mole per liter of 0.008M NaOH solution. The CoCl_2 concentrations varied from 0.00077 to 0.00385 mole per liter of solution. For comparison with the concentration units used in the preceding sections, a CoCl_2 concentration of 0.00385 mole per liter of solution is equivalent to a concentration of 0.00688 mole CoCl_2 per mole NaBH_4 , in a 0.56M NaBH_4 solution.

Table 12 summarizes the rate data obtained. The third column lists the values for k_1 , which is the first-order rate constant, and the fourth

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TABLE 12. SUMMARY OF THE RATE DATA OBTAINED

	CoCl ₂ ,		
Temperature, C	mole/liter of solution	k ₁ , min ⁻¹	k _h , min ⁻¹
<hr/>			
NaBH ₄ = 0.13 mole/liter of solution			
<hr/>			
20	0.00154	0.00759	0.00221
20	0.00232	0.00806	0.00235
20	0.00270	0.00694	0.00202
20	0.00385	0.0208	0.00605
25	0.00154	0.0149	0.00433
25	0.00232	0.0272	0.00792
25	0.00308	0.0313	0.00911
25	0.00385	0.0463	0.0135
30	0.00154	0.0477	0.0139
30	0.00308	0.0868	0.0253
30	0.00385	0.0981	0.0285
35	0.00154	0.0716	0.0208
35	0.00232	0.140	0.0407
35	0.00308	0.195	0.0567
35	0.00385	0.177	0.0515
NaBH ₄ = 0.26 mole/liter of solution			
<hr/>			
20	0.00077	0.00107	0.000476
20	0.00154	0.00430	0.00191
20	0.00232	0.0097	0.00431
20	0.00385	0.0131	0.00583
25	0.00077	0.0039	0.00174
25	0.00154	0.0125	0.00556
25	0.00232	0.0152	0.00676
25	0.00385	0.0240	0.0107
30	0.000385	0.0055	0.00245
30	0.00077	0.0108	0.00481
30	0.00154	0.0392	0.0174
30	0.00232	0.0346	0.0154
30	0.00385	0.0622	0.0277
35	0.00077	0.0168	0.00748
35	0.00154	0.0359	0.0160
35	0.00232	0.0562	0.0250
35	0.00385	0.0806	0.0359

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TABLE 12 (Continued)

Temperature, C	CoCl ₂ , mole/liter of solution	k ₁ , min ⁻¹	k ₂ , min ⁻¹
<u>NaBH₄ = 0.56 mole/liter of solution</u>			
20	0.00385	0.00922	0.00648
20	0.00385	0.0112	0.00787
25	0.00077	0.00064	0.00045
25	0.00154	0.00485	0.00341
25	0.00232	0.0106	0.00745
25	0.00385	0.0157	0.0110
25	0.00385	0.0145	0.0102
25	0.00385	0.0150	0.0105
25	0.00385	0.0187	0.0131
25	0.00385	0.0184	0.0129
30	0.00385	0.0327	0.0230
30	0.00385	0.0311	0.0219
35	0.00385	0.0369	0.0259
35	0.00385	0.0383	0.0269

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column, the values of k_h , which is the heterogeneous rate constant. The latter will be referred to in more detail subsequently. Thus, k_1 is the rate "constant" that is proportional to the concentrations of CoCl_2 and NaBH_4 ; k_h is the rate constant which takes into account the rate change effected by the NaBH_4 concentration.

Analysis of the Data

Figure 9 presents a typical rate curve showing the behavior of the hydrolysis as a first-order reaction with respect to the NaBH_4 concentration. The slight deviation early in the reaction is a typical effect which has been observed in most of the rate experiments. It is probably related to the formation of the true catalyst, and to the time delay involved in the uniform dispersion of the catalyst throughout the solution, as is discussed later.

Figure 10 shows the proportionality of the first-order rate constant to the CoCl_2 concentration. Figure 10 probably represents a better example of this proportionality than was generally found in these studies; in general, there was more scatter in the data.

It may be observed in the data of Table 12 that, at constant temperature and constant CoCl_2 concentration, the first-order rate constant decreases as the NaBH_4 concentration increases. For example, at 25 C (77 F) and a CoCl_2 concentration of 0.00385 mole per liter of solution:

<u>NaBH_4 Concentration, mole/liter of solution</u>	<u>First-Order Rate Constant, k_1, min^{-1}</u>
0.13	0.046
0.26	0.024
0.56	0.016

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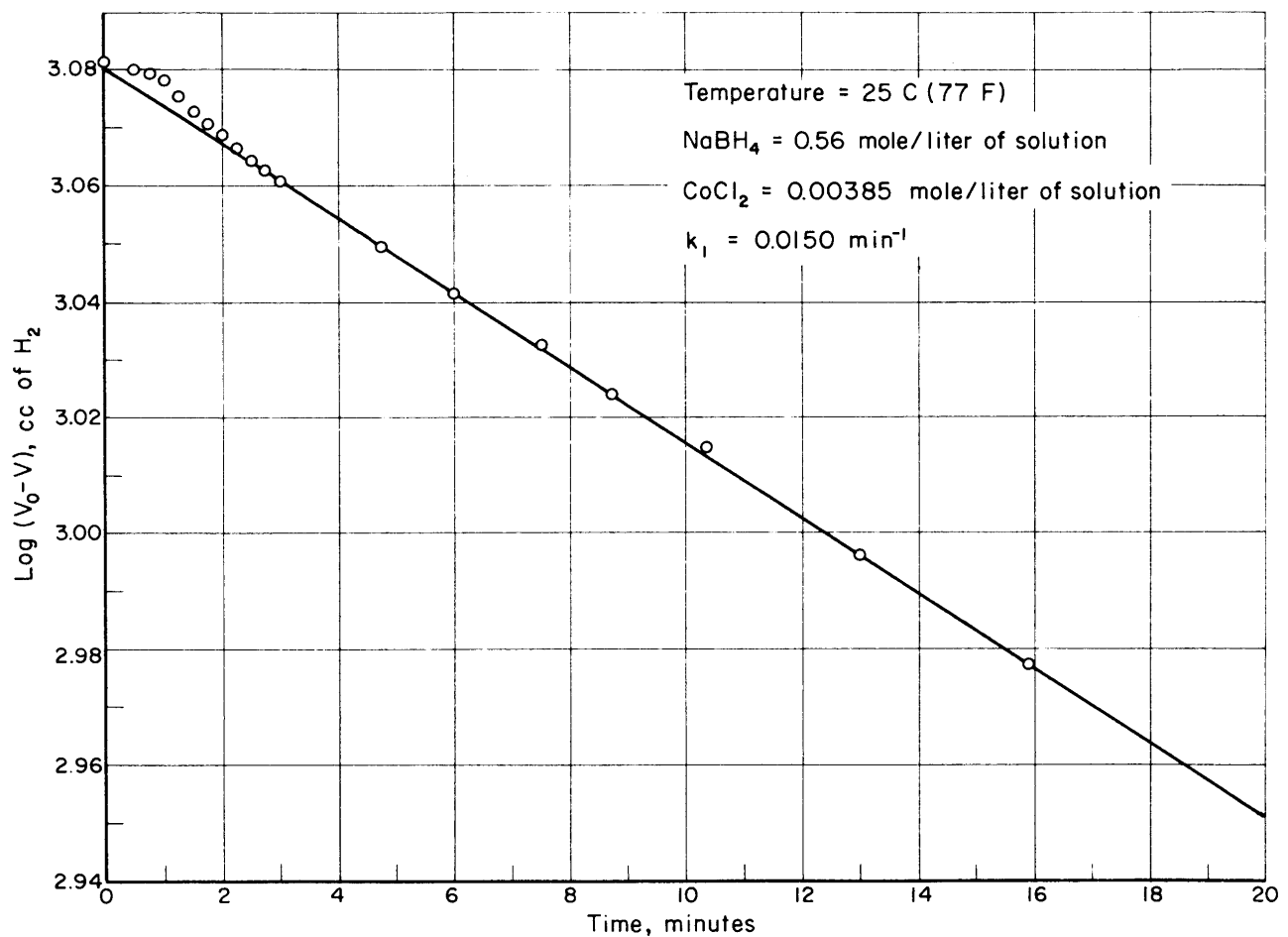


FIGURE 9. FIRST-ORDER PLOT FOR NaBH_4 HYDROLYSIS

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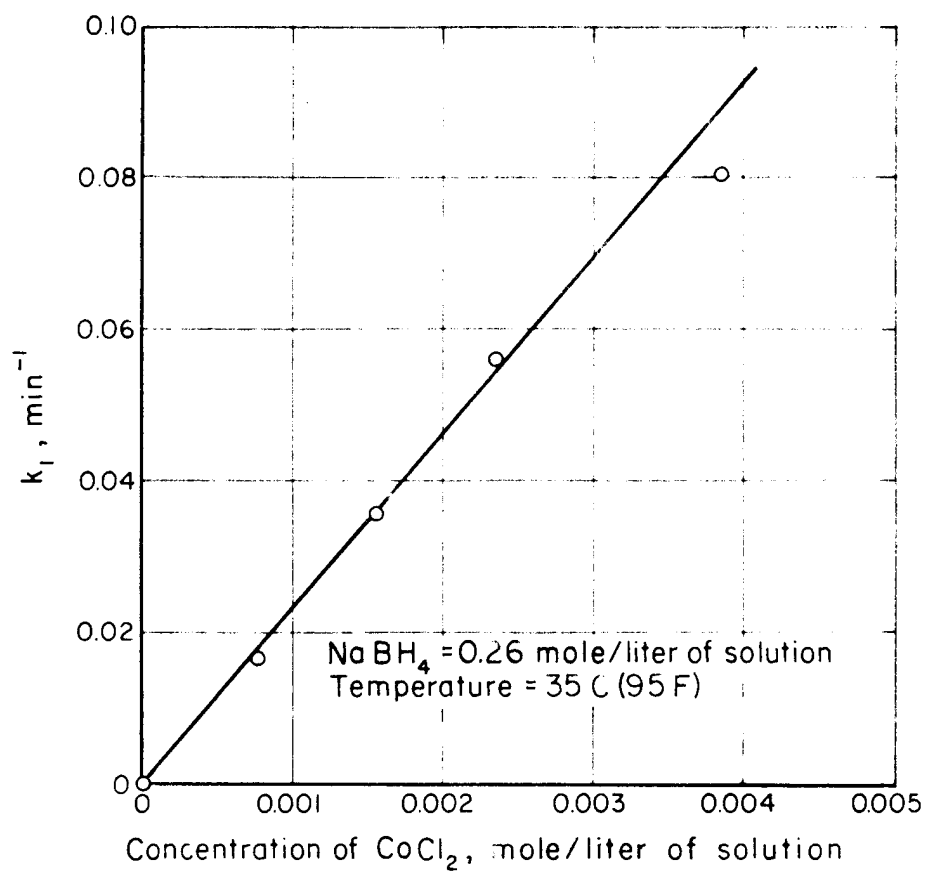
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FIGURE 10. VARIATION OF k_1 WITH CoCl_2 CONCENTRATION

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It appears, therefore, that the unimolecular hydrolysis reaction is actually a first-order reaction for some activated complex which is formed on the surface of the catalyst, and that the first-order rate constant is a function of the NaBH_4 concentration. If it is assumed that the first-order rate constant varies inversely with some power of the NaBH_4 concentration, in the manner:

$$k_1 = k_n / (\text{NaBH}_4)^m,$$

then k_n should be independent of the NaBH_4 concentration. The first-order rate equation for a given CoCl_2 concentration:

$$\frac{d\text{H}_2}{dt} = k_1 (\text{NaBH}_4)$$

then becomes:

$$\frac{d\text{H}_2}{dt} = k_n (\text{NaBH}_4)^n,$$

where $n = 1-m$.

An approximate value for m , obtained by fitting the kinetic data to the above equation, is 0.61. The exponent n therefore equals 0.39.

Figure 11 is a plot of the same rate data as were shown in Figure 9, but is based on the rate varying as the NaBH_4 concentration to the 0.39 power. As was stated, k_n should be, and is, independent of the NaBH_4 concentration; the k_n values corresponding to the k_1 values which were listed previously and shown to vary inversely with the NaBH_4 concentration are 0.014, 0.011, and 0.012, respectively.

Figure 12 shows the variation of k_1 with temperature. It is quite apparent that the precision of these data is not very high.

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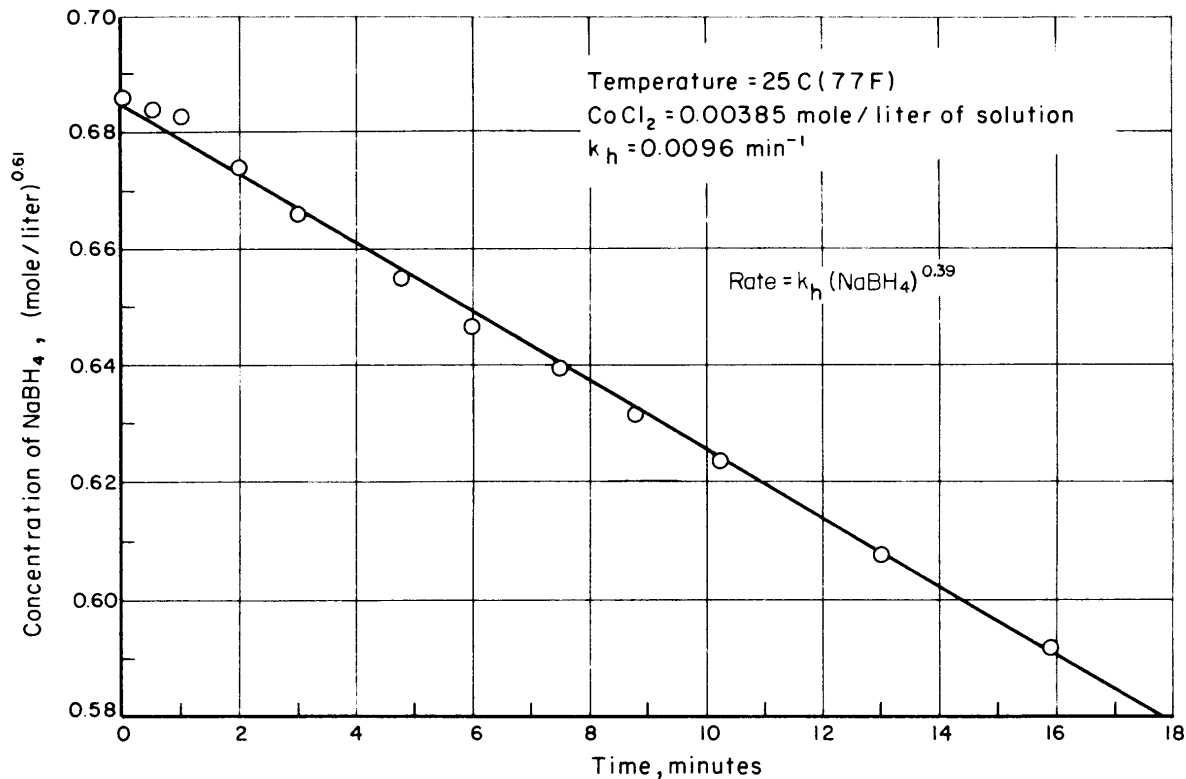
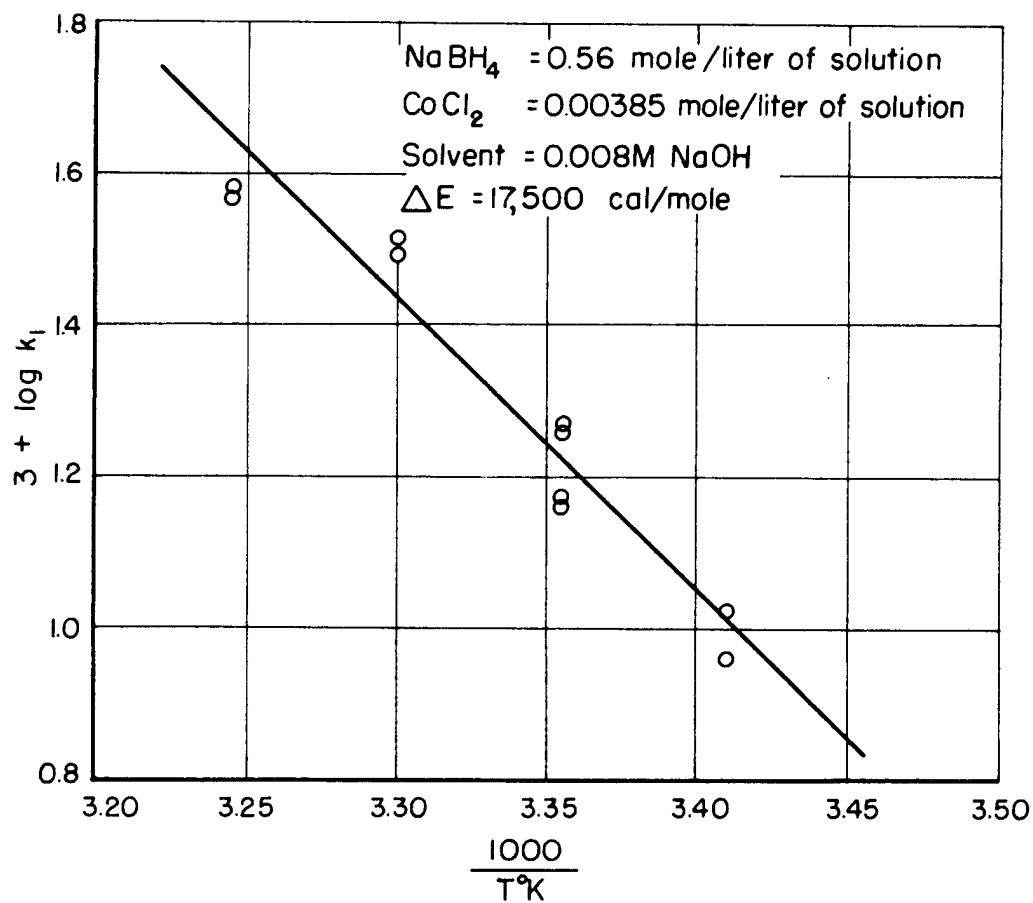


FIGURE II. DERIVATION OF HETEROGENEOUS RATE CONSTANT, k_h 0-22458

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FIGURE 12. VARIATION OF k_1 WITH TEMPERATURE

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The activation energies calculated from the data relating reaction rate to temperature are as follows:

<u>NaBH₄ Concentration, mole/liter of solution</u>	<u>Activation Energy, cal/mole</u>
0.13	29,500
0.26	23,000
0.56	17,500

It is of interest that there appears to be some variance in the activation energy depending on the NaBH₄ concentration. The reason for this has not been pursued since the primary effort under Task Order No. C was not concerned with kinetic studies but with the actual development problem. The value of 17,500 cal per mole has been used in subsequent calculations to permit a comparison of the kinetic data with those pertaining to the full-scale reactor.

Mechanism Studies

Earlier, with the aid of Figure 2, a general description of the manner in which the reaction proceeds was presented. Briefly, it was stated that as soon as the CoCl₂ was added a black precipitate was formed; and that a rather sharp increase in the temperature of the system, and also, although less sharp, an increase in the amount of hydrogen evolved were observed during the early stages of the reaction. In Figures 9 and 11 it will also be noted that some phenomena are occurring within the first two minutes of these reactions, and these may be some preliminary reaction(s). If the CoCl₂ were the catalyst for the preliminary reaction(s), there would be no sharp changes

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in the rate curve during the first few minutes; however, since sharp changes were noted, it is possible that there is a preliminary reaction in which cobalt boride or some cobalt-boron product is formed which is the true, heterogeneous catalyst.

A few experiments directed toward an investigation of these early reactions were performed in an attempt to establish whether the evolution of some hydrogen at the start of the reaction in the full-scale generator might present a serious problem. During the first few minutes of the reaction, apparently cobalt boride is being formed, hydrogen is being evolved, and a heat of reaction develops that is exothermic and therefore raises the temperature of the system by one or two degrees. In the full-scale-generator operation a rather large amount of hydrogen could be evolved under these conditions.

Table 13 presents data from two experiments in which dilute NaBH_4 solutions were reacted with excess CoCl_2 . As the data show, the hydrolysis reaction was very fast - actually too fast to follow by means of ordinary techniques.

In the first experiment, 2.3 mmole H_2 was produced from 0.79 mmole NaBH_4 , or 2.9 moles H_2 per mole NaBH_4 . In the second experiment, 7.3 mmole H_2 was evolved from 2.35 mmole NaBH_4 , or 3.1 moles H_2 per mole NaBH_4 .

The solution resulting from the second experiment was filtered in air, and the black precipitate which had formed during the reaction was collected on filter paper. The precipitate was dried overnight in an oven at 110 C and then weighed; the weight was 104.4 mg. The precipitate was then analyzed for cobalt and boron by our Analytical Chemistry Division. The

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TABLE 13. DATA FROM THE REACTION OF NaBH_4 WITH EXCESS CoCl_2

Experiment I (0.79 mmole NaBH_4)		Experiment II (2.35 mmole NaBH_4)	
Time, min	H_2 , mmoles	Time, min	H_2 , mmoles
<0.5	1.9	<1	7.0
1	1.9	2	7.1
2	2.0	3	7.3
7	2.2	7	7.3
11	2.3	26	7.3
33	2.3	29	7.3

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results showed 78 mg of cobalt and 6.4 mg of boron, totalling only 84.4 mg and leaving 20 mg unaccounted for. These results indicate that the precipitate contained 1.3 mmoles of cobalt and 0.59 mmole of boron. Therefore, the product apparently contains 2 moles of cobalt per mole of boron; this confirms the results of Schlesinger and his group⁽³⁾, that the active catalyst is a 2:1 cobalt-boron compound.

It has been reported that the black cobalt boride precipitate is pyrophoric in air. If so, it would be expected that, when handled as described above, the black precipitate would have oxidized during the drying period or possibly even while in the aqueous solution. If it is assumed that the 20 mg unaccounted for represented oxygen, the following interpretation of the chemical-analysis data can be made:

Weight of sample	104.4 mg
Chemical analysis: B	6.4 mg (0.59 mmole)
Co	78 mg (1.3 mmoles)
Unaccounted-for weight:	20 mg
Co required to form CoB =	34.9 mg (0.59 mmole)
Therefore, Co available to form CoO ₂	= 43.1 mg (0.73 mmole Co)
If the 20 mg unaccounted for is O ₂ , then 20 mg should be equivalent to the amount of O ₂ required to form CoO ₂ ;	

$$\frac{20}{32} = 0.62 \text{ mmole O}_2$$

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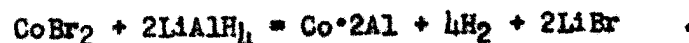
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Thus, the analytical check is reasonably close. It is, therefore, concluded that the analytical data support but do not necessarily confirm the hypothesis that the precipitate analyzed was a mixture of CoB and CoO₂, but this is not necessarily the true catalyst.

This reaction of NaBH₄ directly with CoCl₂ is so complex that at present a balanced stoichiometric equation for it cannot be written. It is believed, from this cursory study, that NaBH₄ reacts with CoCl₂ in the initial stages of the hydrolysis to form a black product which appears to be made up of cobalt boride (CoB) plus free cobalt, and that 3 moles of hydrogen are evolved per mole of NaBH₄.

A paper has been published recently on the reaction of CoBr₂ with LiBH₄ and LiAlH₄ in diethyl ether⁽⁷⁾. Stewart and Schaeffer report a H₂/LiAlH₄ ratio of 1.92 in reactions with excess CoBr₂ (they do not report on comparable reactions with LiBH₄) and the formation of a precipitate referred to as Co·2Al. The Task Order No. C studies yielded a H₂/NaBH₄ ratio of 3 and a precipitate which contained two moles of Co and one mole of B.

Stewart and Schaeffer's results indicate fairly positively that their reaction proceeds as follows:



They report a comparable reaction for LiBH₄.

The results of the studies described are not in agreement with the above; however, the reactions are not necessarily comparable, since water is a reactive solvent in the catalyzed hydrolysis of NaBH₄. The elemental formula of the black precipitate, Co₂B, is fairly well established by the

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work of Schlesinger⁽³⁾ and of the Task Order No. C study. It is not possible at present, however, to set down a series of stoichiometric equations which permit a quantitative explanation of the current data.

The current data do indicate a fairly good 1:1 stoichiometric relationship between the amount of boron found in the catalyst and that which was available in the NaBH_4 , on the basis of Experiment II of Table 13. The previously described analysis accounted for 0.59 mmole of the original 0.67 mmole of boron in the NaBH_4 .

The information obtained from these mechanism studies is exceedingly fragmentary, and no final postulations can be made as to the actual mechanism which produces the true catalyst in this system. The data obtained are of value, however, since they give an indication of the amount of hydrogen which may be expected to evolve from the reaction in the generator as soon as the CoCl_2 is added to the system. Using the molar ratio of 3 moles of hydrogen per mole of NaBH_4 , as found in these reactions, and using a CoCl_2 concentration of 0.006 mole per mole of NaBH_4 , it is calculated that approximately 0.4 cu ft of hydrogen per cu ft of solution will be evolved. This approximation is based on a 1:1 molar reaction of CoCl_2 with NaBH_4 and a borohydride concentration of 0.56 mole per liter of solution. With reference to the "pool" design mentioned earlier, at this catalyst concentration about 30 cu ft of hydrogen would be evolved initially from 75 cu ft of solution.

ENGINEERING ANALYSIS OF SYSTEM

The data presented and the analyses described thus far indicate the

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feasibility and flexibility of the two-solution $\text{CoCl}_2\text{-NaBH}_4$ system for the intended application. It has been shown that for charge sizes up to 36.4 cu ft of hydrogen, generators can be constructed to produce hydrogen at various generation rates. It is now necessary to translate the results of these studies into data pertaining to the full-scale generator.

The bulk design of the generator was established (following consultation with the Sponsor) as a pool of solution 1.5 ft deep with 50 sq ft of surface area. The next step was to establish the parameters of concentration and temperature, and the procedure of operation for the full-scale generator. Of interest in this connection is the establishment of the effects of four factors: (1) temperature, (2) CoCl_2 concentration, (3) NaBH_4 concentration, and (4) natural-water contaminants. The last effect has been analyzed and discussed earlier. The first three effects are analyzed below.

Calculated Rates of Generation

On the basis of the temperature-dependency studies, it can be shown that the rate of generation may be expressed as:

$$\frac{d\text{H}_2}{dt} = A(\text{NaBH}_4)^{0.39} e^{-17,500/RT}$$

The accuracy of the specific parameters in this equation is questionable. However, theoretical rate curves can be calculated using this equation, and these can be compared with experimental rate curves.

Figure 13 is a compilation of one experimental and four theoretical rate curves. The theoretical rate curves were calculated from the rate

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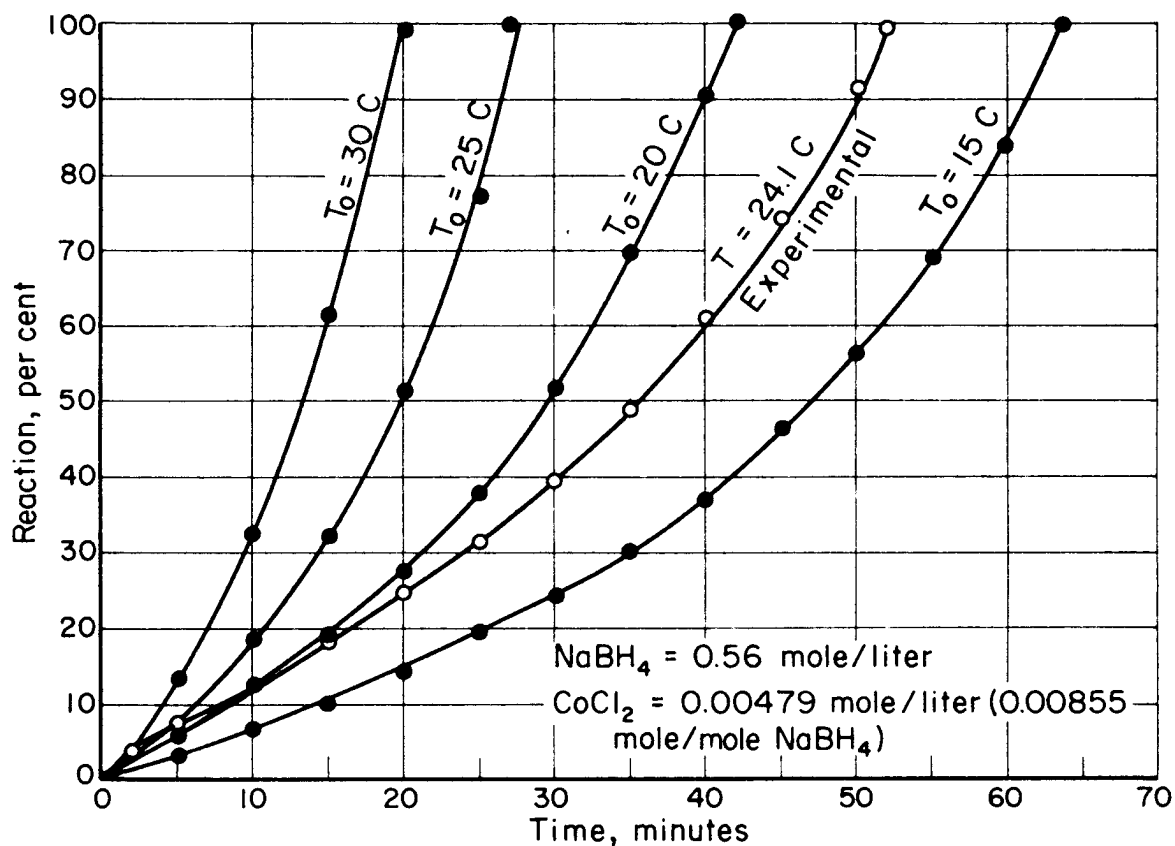


FIGURE 13. THEORETICAL GENERATION RATE CURVES—EFFECT OF INITIAL TEMPERATURE

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equation shown above. The values of the parameters used in these calculations were:

NaBH_4 concentration	0.56 mole/liter
CoCl_2 concentration	0.00479 mole/liter
A (collision factor)	$10^{10.85}$
ΔE	17,500 cal/mole
ΔH	57,500 cal/mole

The reaction was assumed to be adiabatic, and the calculations were made over 5-minute intervals of time.

The experimental rate curve in Figure 13 is the same as that shown in Figure 7 for the 36.4-cu-ft charge which was not insulated. As was mentioned earlier, this curve does not represent a completely adiabatic experiment.

It is to be noted that the experimental curve does not fall in the expected position among the theoretical curves. There are several factors which account for this. Two factors, mentioned above, are the inaccuracy of the kinetic parameters and the "nonadiabatic" conditions of the experimental run. These factors, however, may not represent the entire explanation.

The major factor is probably related to a difference in the rate constants obtained in the kinetic studies and in the aliquot-scaling studies. It will be recalled that the addition of catalyst solution to the borohydride solution was made in most of the aliquot experiments at a ratio of 1 to 30 volumes, respectively. In the kinetic studies, on the other hand, the ratio has been 1 to 4 volumes. The high activation-energy value obtained from the kinetic studies indicates that the catalysis is not diffusion-controlled. Due

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to the completely different geometry of the large-scale reactors and the different ratios of the volumes of the solutions, the catalysis in the large-scale reactors probably differs from that in the small reaction flask used in the kinetic studies. It is quite probable that the large-scale reaction, at least during the first 5 to 10 minutes, proceeded at a much slower rate than did the kinetic-study reactions because the cobalt boride was not distributed uniformly throughout the reacting solution as rapidly in the former. As a result, the rate constant used in calculating the theoretical curves is probably higher than the constant that pertains to the larger scale experimental runs.

Table 14 shows the effect of the initial reaction temperature on the generation rate for an adiabatic system. The calculations indicate that, for temperature increases of 5 degrees C (9 degrees F), an approximate increase of 50 per cent occurs in the over-all reaction rate in an adiabatic system, as compared with an approximate increase of 65 per cent for the rate constant k_h . The temperature effect has been pointed out qualitatively in previous discussions of experimental rate data (for example, Figure 7) and is shown here quantitatively. Since the initial temperature of the natural waters used in the field can easily vary by more than 5 degrees C (9 degrees F), the temperature effect is important in the operation of the proposed full-scale generator.

Figure 14 shows the effect of catalyst concentration on the adiabatic generation rate.

The rate constant has been shown to vary proportionally with the CoCl_2 concentration in the isothermal, kinetic studies (see Table 12). Table 15

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TABLE 14. DATA ON THE EFFECT OF TEMPERATURE ON HYDROLYSIS RATES

(Reaction conditions: Adiabatic reaction; NaBH_4 - 0.56 mole/liter; CoCl_2 - 0.00479 mole/liter)

Initial Temperature, C	Time for Complete Reaction		k_h	
	Minutes	Ratio	Minute ⁻¹	Ratio ⁻¹ *
15	64	1.52	0.00436	1.70
20	42	1.50	0.00742	1.61
25	28	1.40	0.0119	1.64
30	20		0.0195	

*Reciprocal of the ratio of k_h for the higher temperature to k_h for the lower temperature.

TABLE 15. DATA ON THE EFFECT OF CATALYST CONCENTRATION ON HYDROLYSIS RATE

(Reaction conditions: Adiabatic reaction; NaBH_4 - 0.56 mole/liter; initial temperature 25 C)

CoCl_2 , mole/liter	Time for Complete Reaction, minutes
0.00479	28
0.00385	32
0.00300	41

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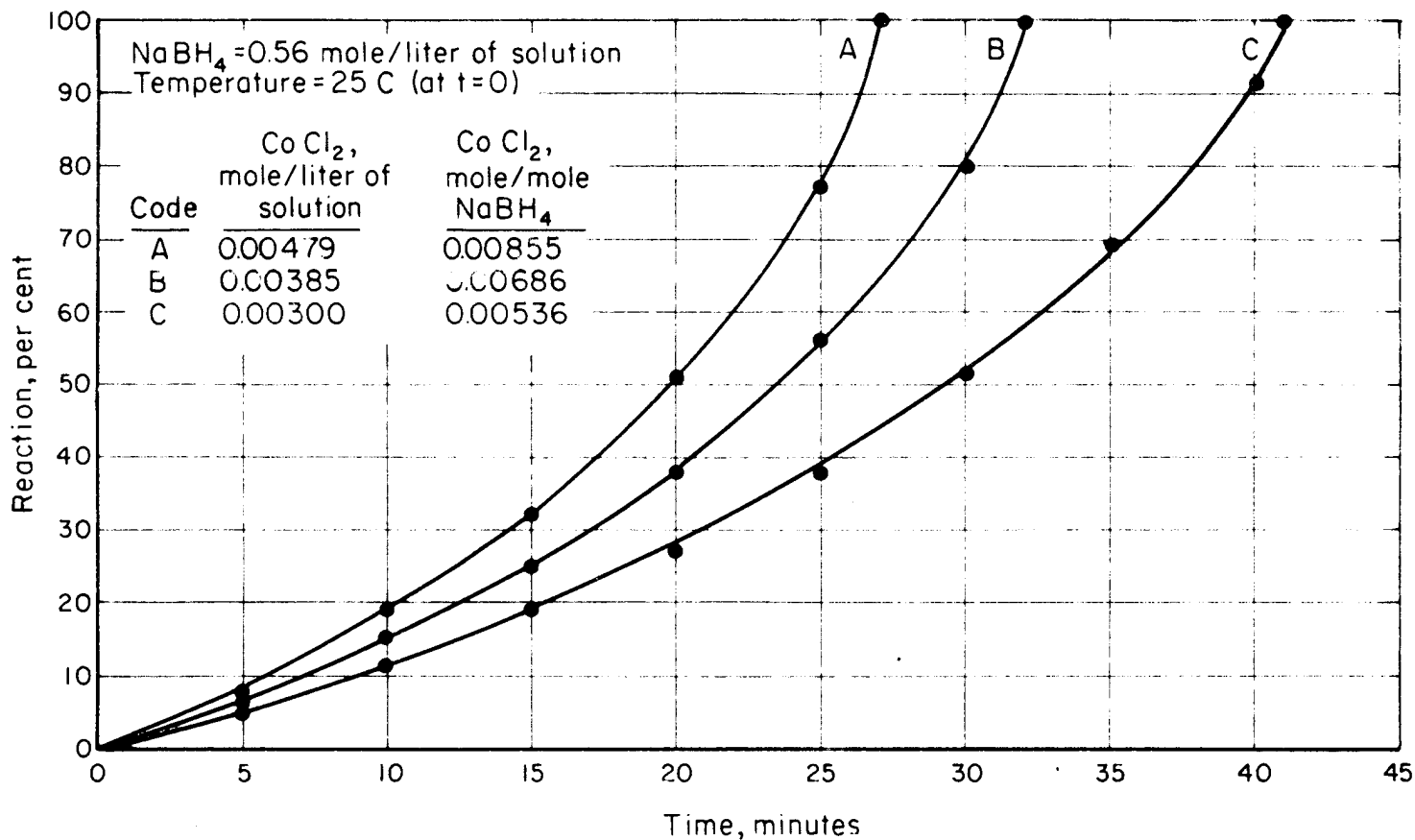


FIGURE 14. THEORETICAL ADIABATIC GENERATION-RATE CURVES-EFFECT OF CATALYST CONCENTRATION

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shows that the time required for generation under adiabatic conditions is also proportional to the CoCl_2 concentration.

Figure 15 shows the effect of NaBH_4 concentration on the adiabatic reaction-rate and temperature-rise curves. The principal factor in choosing the borohydride concentration for the proposed full-size generator is the allowable temperature rise. Since the heat of reaction, ΔH , is 57.5 kilocal per mole, the temperature rise in an adiabatic system is:

$$\Delta T = (57.5)(C)$$

where C is the initial NaBH_4 concentration in moles per liter.

It is of interest to note in Figure 15 that, up to about 60 per cent reaction, the more concentrated solution evolved hydrogen at a slightly slower rate, but then it reacted more rapidly as additional heat was absorbed by the system. It may be concluded from Figure 15 that the effect of borohydride concentration, at least in the range examined here, on the reaction-rate curves is not appreciable; and that, if a smaller over-all generator that had the same hydrogen-generation capacity were desired, the borohydride concentration could be increased (e.g., by using a similar amount of NaBH_4 and less water) and, thus, such a device could be achieved.

The theoretical rate curves shown in this section should all be accepted as preliminary and somewhat speculative predictions when they are discussed in light of the experimental results. They do explain the effects of temperature, and of catalyst and borohydride concentration, at least as a first approximation. A program could be set up to obtain a direct relation between the kinetic studies and the large-scale studies. However, such a

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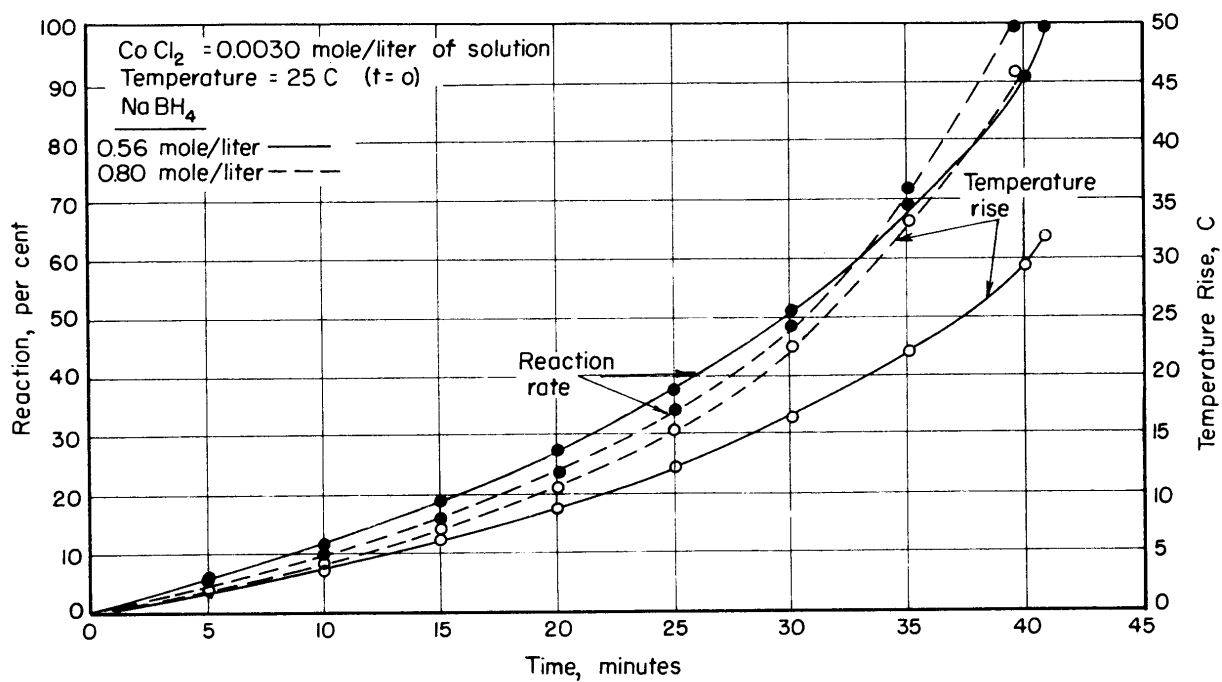


FIGURE 15. THEORETICAL GENERATION-RATE AND TEMPERATURE-RISE CURVES - EFFECT OF BOROHYDRIDE CONCENTRATION

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study is beyond the scope of this program. If the kinetic and the large-scale studies were more directly related, it would have been worth while to carry on these calculations in greater detail, that is, to set up these calculations as a machine operation, and to run the entire gamut of the effects of temperature, catalyst concentration, and borohydride concentration.

The calculations described in this section have shown the relative effects of temperature, catalyst concentration, and borohydride concentration. The importance of these factors appears to be in the order indicated. For adiabatic systems, a 5-degree-C variation in reaction temperature causes about a 50 per cent change in the over-all reaction rate. The catalyst and borohydride concentrations, within limits, have been shown to contribute to the temperature rise of the system and not directly to a change in the over-all reaction rate.

In the operation of a full-size generator, it will be necessary for the operator to determine the temperature of the borohydride solution before adding the catalyst solution, since the amount of catalyst solution to be added will depend upon this temperature.

Table 16 presents a listing of the amount of CoCl_2 needed when water with various starting temperatures is used. These weights were calculated on the basis of a 5-degree-C change of temperature effecting a 50 per cent change in the total reaction rate, and also on the basis that the rate of reaction varies proportionally with the catalyst concentration, even under adiabatic conditions. The data in Table 16 were obtained using the following equations:

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TABLE 16. WEIGHTS OF CoCl_2 NEEDED AT
VARIOUS INITIAL TEMPERATURES
IN FULL-SCALE OPERATION

Temperature		Amount of CoCl_2 , pounds
C	F	
15	59.0	4.4
20	68.0	2.8
22	71.5	2.4
25	77.0	1.9
30	86.0	1.3

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$$\text{CoCl}_2, \text{ pounds} = 5.13 \times 10^{-11} e^{-\frac{7,250}{T}},$$

where T is expressed in degrees Kelvin.

This equation was obtained in the following manner. On the basis of the kinetic studies, it can be shown that the rate constant depends upon the CoCl_2 concentration and the temperature as follows:

$$k \propto (\text{CoCl}_2)(e^{-17,500/RT})$$

Changes in the temperature and/or CoCl_2 concentration can be compensated for by maintaining the right-hand side of the above relationship constant. The isothermal studies, however, indicated that the expression $e^{-17,500/RT}$ is too high for the adiabatic system, that is, a 5-degree-C change in the reaction temperature causes only a 50 per cent change in the total reaction time rather than a 65 per cent change. To adjust for this, the value for the activation energy was reduced to 14,500 calories per mole. With an initial temperature of 22 C (72 F) and a CoCl_2 weight of 2.4 pounds taken as the reference points in calculating a value for k, the above-indicated equation was obtained.

THE PRELIMINARY HYDROGEN-GENERATOR DESIGN

As a result of the foregoing research, it has been possible to develop a preliminary design of an extremely simple hydrogen generator. The preliminary design evaluation and the results are described below.

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Original Concept of the Hydrogen Generator

At the start of the program, it was thought that all of the ultimate preliminary generator designs would be of two basic types: (1) those using the flow process, and (2) those using the batch process. Because it was believed at that time that the water for the generator might have to be transported to the generating site, the flow-process type of design seemed to offer several attractive features. Unfortunately, however, the design of a generator using the flow process would be somewhat complicated. A hand-powered pump of some type would be needed to supply water to the generator. Some type of heat exchanger would be required to reduce the temperature of the solution and of the hydrogen gas produced. A device would be needed to control the rate of generation, and a drying apparatus would be required to remove water vapor from the comparatively warm hydrogen. It was anticipated that such a generator would contain several metal parts and would probably weigh very close to 400 pounds. Fortunately, changes in the proposed operating procedure, as described below, made possible the design of a much simpler and lighter generator.

Changes in Operating Procedure

During a discussion of the problems of hydrogen generation with the Sponsor, it was indicated to us that the generating apparatus could ordinarily be erected near a natural body of water which would be at least 10 feet square and 2 feet deep. This new concept in operating procedure made possible a major shift in our thinking, because it meant that the entire amount of water needed would not only be at hand, but also that the proposed

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generator could actually be placed in the water for operation.

With the proposed generator surrounded by water, there would be no force from the contained water on the sides or bottom of the generator, and only a thin plastic material would be needed to separate the reaction solution in the generator from the surrounding water. It then became possible to envision a design which would use the batch process and be very lightweight.

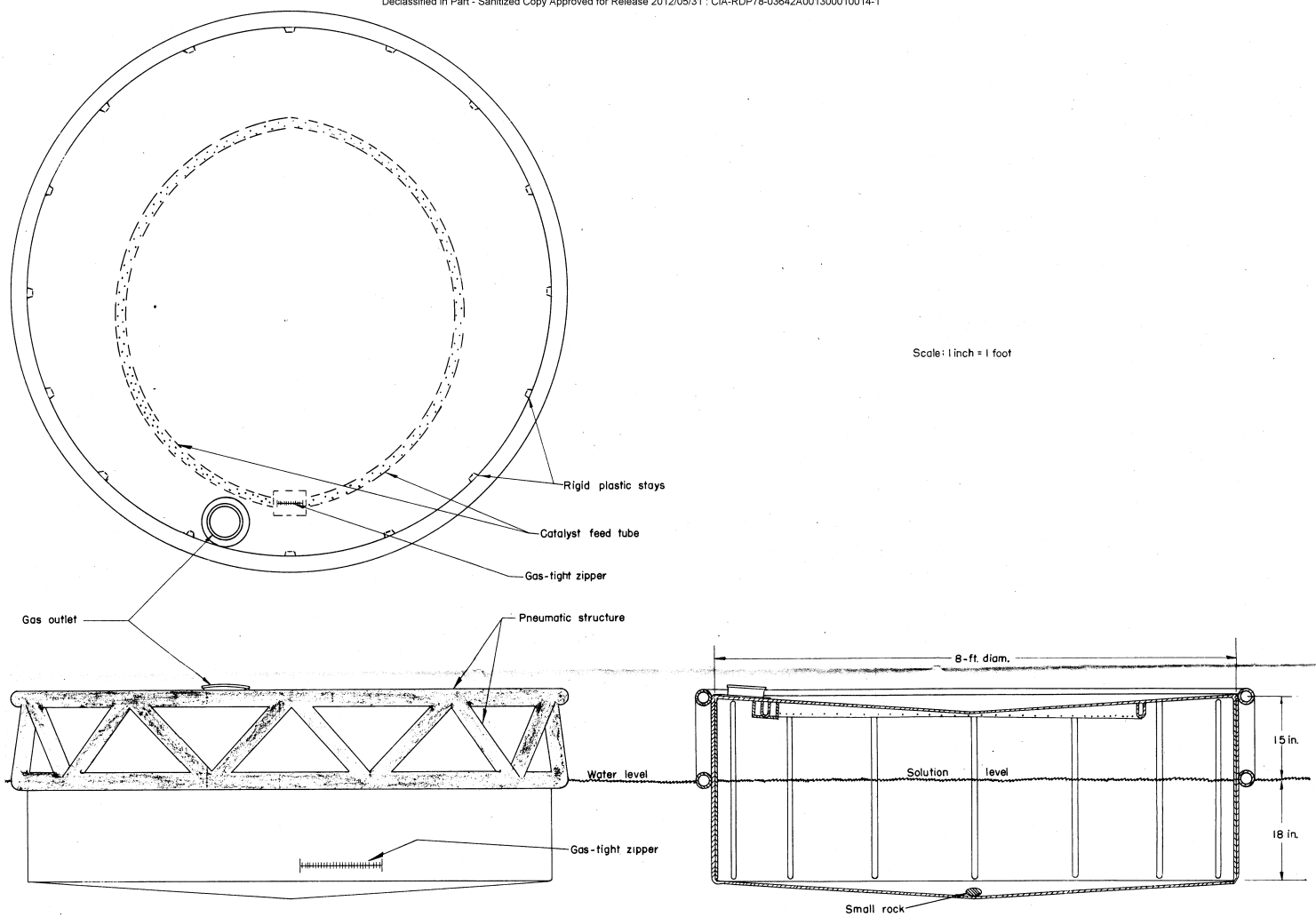
Furthermore, during discussions with the Sponsor, it was agreed that the gas-drying device could be eliminated because the major part of any trapped water vapor would condense and drip out of the open bottom of the balloon, and extra hydrogen could be produced to make up for the weight of the condensate remaining in the balloon.

These changes in operating procedure made it possible to consider the use of a simple, lightweight plastic container which would have built-in plastic zippers and would be extremely simple to set up and use. Thus, design efforts have been directed almost entirely toward such a generator.

Preliminary Design of Proposed Generator

Figure 16 shows three views of the preliminary design of the proposed generator. The unit would be a pneumatically supported structure 33 inches in height and 8 feet in diameter. During operation, it would be submerged in the water to a depth of 18 inches by the weight of the reaction solution; the top 15 inches would be supported above the water to allow space for the foam generated during the reaction.

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FIGURE 16. THREE VIEWS OF PRELIMINARY DESIGN OF PROPOSED HYDROGEN GENERATOR

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The NaBH_4 would be put into the generator through the gas outlet, one gas-tight zipper would be used to permit water to flow in and fill the generator, and a second zipper would be used to permit the addition of the catalyst solution which had been pre-mixed in a container that had been supplied. One circular tube, which was perforated at several (number to be determined) uniformly dispersed points, would distribute the catalyst solution and facilitate its uniform addition to the borohydride solution. The gas outlet, bonded to the top of the unit, would facilitate the attachment of the balloon.

Numerous instances of pneumatic structures have been found in the literature. These have varied from dummy guns, tanks, and landing craft to immense balloon-like structures housing radar stations. Of the materials used for these structures, the one involved in the "radar stations" is perhaps the most relevant, as the following quotation⁽⁸⁾ shows.

"Much research has been spent on finding the best materials for construction of the envelope. The design called for a fabric which was strong and weather resistant, would not stiffen in extreme cold, would not absorb moisture, would not stretch too much yet would give when necessary, could be stored for long periods without deteriorating, and, above all, would not significantly absorb radio energy, so that radar signals could pass through the envelope freely. The principal fabrics investigated so far have been Fiberglas, nylon, Fortisan (a rayon), and Dacron. Field experience has shown that for radomes, the best of these are nylon and Dacron. To improve resistance to tearing, the fabrics are used in a two-ply weave with the threads biased at a 45-degree angle; when this is punctured, it

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does not rip beyond the original break.

"For resistance to weathering, the fabric is coated with neoprene containing a little carbon black. A vinyl-base white paint over this coating proves effective in improving resistance to weather and in reflecting the sun's heat, but in severe climates, the radome had to be repainted as often as every year. Further development produced a paint known as Radolon (chlorosulfonated polyethylene) which has given the best service of any so far."

It is believed that the entire generator could be made in one piece from materials similar to those described and would have a total weight of 50 pounds or less. The actual details of construction of the generator are not fixed at this time. For instance, the pneumatic-tube structure can be made in more than one way and the location of the stays could be different from that shown in Figure 16. However, it is believed that a one-piece generator based on the ideas shown in Figure 16 could be built, and that the best configuration could be established by conferences with manufacturers such as The Goodyear Tire and Rubber Co.

Possible Operating Procedure

The operating procedure is expected to be approximately as follows:

- (1) Unpack the generator kit
- (2) Inflate (by CO₂ or by air from the mouth or hand pump)
while the structure is on the water or as near to the
water as possible

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- (3) Put small stone inside on the bottom to hold unit down
- (4) Open side zipper and allow water to flow in
- (5) Close side zipper when water no longer flows in
- (6) Put sodium hydroxide in through gas outlet
- (7) Mix the solution by rocking the generator and causing the contents to slosh back and forth
- (8) Put sodium borohydride in through gas outlet
- (9) Mix again as in Step 7
- (10) Attach balloon
- (11) Take water temperature
- (12) Consult chart (CoCl_2 concentration or weight versus water temperature)
- (13) Mix proper amount of catalyst in water and pour solution in through top zippered opening
- (14) Close zipper
- (15) Tend balloon.

Fulfillment of Design Specifications

It appears at this time that a hydrogen generator could be constructed that would comply with all of the design specifications originally set up. Furthermore, from the standpoint of low weight and simplicity of operation, it appears that the proposed generator would be extremely satisfactory. The specifications would probably be met as described below:

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- (1) Capacity. Enough hydrogen, i.e., about 3,500 cu ft, could be provided to obtain 250 pounds of lift at sea level.
- (2) Rate. Total capacity would be generated at a controlled rate within 1 hour.
- (3) Pressure. Calculations show that the hydrogen pressure at the outlet would be approximately 0.4 psi.
- (4) Temperature of Off-Gas. The temperature of the off-gas would be no greater than about 90 degrees F (50 degrees C) above the temperature of the water.
- (5) Maximum Weight. The total weight of the chemicals, exclusive of the water, and the generator would be approximately 158 pounds, which is well below the maximum specified, namely, 500 pounds.
- (6) Construction. Radar detectability would be extremely low because of the nonmetallic nature of the materials. The entire generator would be one piece and would weigh approximately 50 pounds.
- (7) Operation. The generator could easily be operated by one nontechnical operator. Furthermore, he would have ample time to tend the balloon. The absence of metal parts should greatly reduce the possibility of an explosion.
- (8) Durability. It appears that the proposed generator could be shipped quite safely and stored for a period of many months.

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(9) Auxiliary Power and Materials for Operating Satisfactorily.

Water would be the only material necessary for the operation of the generator.

(10) Costs. Although cost estimates have not been obtained for the generator, the cost should be relatively low.(11) Availability. The generator would be very adaptable to production at the facilities of many companies manufacturing plastic products.RECOMMENDED ADDITIONAL DEVELOPMENTS

It would be advantageous for the operator to have some idea of the progress and degree of completion of the reaction. The best way of accomplishing this would be to provide a method of following the rise in temperature during the reaction, in order to make it possible for the operator to note the leveling-off and eventual drop in temperature at the end of reaction.

The "activity" of natural waters, that is, the stability of borohydride solutions in natural waters, is an important aspect of the generator problem. At present, there is no immediate solution to this problem, in that many salts, organic acids, and possibly other impurities, catalyze this reaction. It might be desirable for the operator to have a test kit which he could use to evaluate the "activity" of any natural water before operating the full-scale generator. No test that might be incorporated in a kit has yet been developed for this purpose. One simple test that might be made, however, would be to dissolve about 20 grams of NaBH_4 in about one liter of

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the water (to be used) after some alkaline material had been dissolved in the water. If the solution evolved hydrogen readily, a more basic water solution should be used. This procedure should be repeated until the above test yielded no hydrogen when the borohydride was dissolved in the alkaline water.

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